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AFRPL-TR-68-45

AD389846

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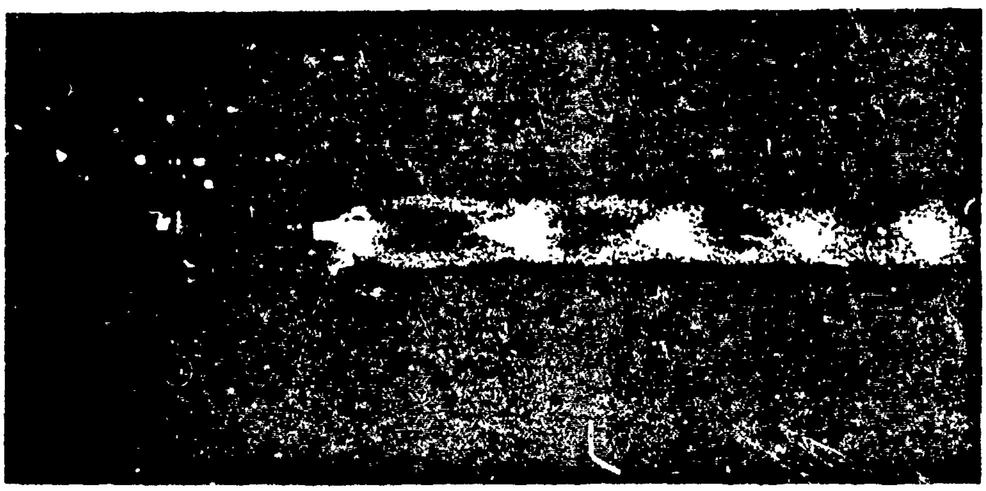
AIR FORCE ROCKET PROPULSION LABORATORY

SEMIANNUAL PROGRESS REPORT (U)

FOR JULY THROUGH DECEMBER 1967
TECHNICAL REPORT AFRPL-TR-68-45



AIR FORCE SYSTEMS COMMAND
UNITED STATES AIR FORCE
EDWARDS, CALIFORNIA

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(U) AIR FORCE ROCKET PROPULSION LABORATORY

(U) SEMIANNUAL PROGRESS REPORT

for

JULY THROUGH DECEMBER 1967

APRIL 1968

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(U) COVER PHOTO

(C) The cover photograph shows the 250,000-lb thrust, 3000-psi staged-combustion thrust chamber test conducted by Pratt and Whitney under AFRPL's Advanced Cryogenic Rocket Engine Program. The engine was tested during Phase I of a two-phase Advanced Development Program to demonstrate a high-performance, throttlable, reusable LO_2/LH_2 rocket engine concept. Eleven test firings at thrust levels from 20 to 100% were conducted to demonstrate performance cooling effectiveness, and combustion stability over a mixture ratio range from 5.0:1 to 7.0:1. Additional information is given in the Liquid Rocket Division Section, Contract AF 04(611)-11401, page 173 .

[redacted]

FOREWORD

This report is the first issue of a series of AFRPL Semiannual Progress reports. This report is intended for distribution to qualified government and nongovernment recipients. This report series supersedes a prior series of AFRPL Quarterly Project Progress Reports which were prepared for government use only.

The Semiannual Progress Report is not only designed to report on the progress of the AFRPL RDT&E program, but to effect an interchange of information (within security limits) with industry and other governmental agencies. Direct contact with AFRPL project engineers is encouraged for this purpose.

This report has been reviewed and is approved.

Elwood M. Douthett

ELWOOD M. DOUTHETT
Colonel, USAF
Commander, Air Force Rocket Propulsion Laboratory

(This page is Unclassified)

UNCLASSIFIED ABSTRACT

This report describes the status and significant progress of each AFRPL contract and in-house laboratory program for the time period of 1 July 1967 to 31 December 1967.

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ROCKET PROPELLANT TECHNOLOGY

LIST OF ACTIVE CONTRACT PROJECTS AND
IN-HOUSE LABORATORY PROGRAMS

PROPELLANT DIVISION (RPC)

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LIST OF ACTIVE IN-HOUSE LABORATORY PROJECTS

(U) Theoretical Calculations on Advanced Oxidizers/United Aircraft Corp./Dr. H.H. Michels/AF 04(611)-11214/Dr. L. P. Quinn (RPCL)

(C) This contract supported AFRPL's research on new rocket propellants by examining the stability of hypothetical propellant molecules, using quantum mechanics. The fluorides, oxides and hydrides of the rare gases were selected for study, with helium, neon and argon being concentrated upon as their low atomic weights make them more attractive from a rocket propellant standpoint.

(U) For the species under consideration, the total energy was calculated by a molecular orbital method with configuration interaction. The variation of energy with bond distance was then examined for any minimum in the curve that would indicate stability. If a molecule appeared to be stable, its energy was also compared to the energy of other potential decomposition fragments, so that instability with respect to these fragments could be determined.

(C) The contract has been completed with the following results and conclusions:

1. The light-element noble gas fluorides appear to show no chemical binding and hence do not offer a promising source of high-energy oxidizers.

2. The hydrides and oxides of argon which were examined show no chemical binding within the limitations of the approximations used and hence, within these limitations, do not appear to have promise as high-energy propellants.

3. The hydrides and oxides of neon do show chemical binding and the molecules in this category with more than one ligand may have potential as possible high-energy propellant sources. The linear dihydride, H_2Ne, appears particularly interesting at this time.

4. The mono- and dihydrides of sodium are both binding, but the dihydride, which might otherwise have propellant applications, appears to be unstable with respect to fragmentation to the monohydride.

5. There are three low-lying bonding states of HB and, of these, the $^3\pi$ state is metastable and capable of yielding a high theoretical specific impulse. The $^1\pi$ state is only very weakly bonding and may be significantly enough perturbed when subjected to isolation in a solid matrix so as to become unstable.

6. There are five low-lying bonding states of HN and, of these, the $^1\Delta$ state is metastable and capable of yielding a high theoretical specific impulse. The $^1\pi$ state of this system is also very weakly bound and hence subject to significant perturbation from ambient fields which could possibly render it unstable.

(U) All of the calculations presented by the contractor were based on gas phase conditions. The development of methods for predicting changes in the energy levels of a system consequent to its introduction into a solid matrix would be extremely useful for practical applications.

LATEST (FINAL) PUBLICATION:

S. B. Schneiderman, "Theoretical Calculations on Advanced Oxidizers", AFRPL-TR-67-283, November 1967, AD 386005.

(U) Ion Chemistry/University of Kansas/Dr. L. J. Kevan/AF 04(611)-11217/Dr. L. P. Quinn (RPCL)

(U) In the search for new sources of energy for rocket propulsion purposes, ionic propellants have been considered many times, since the energies stored (theoretically) could be high. While no promising concept for an ionic propellant exists (ion engines and other low-thrust devices are not under consideration here), the potential remains and the general phenomenon of trapped charged particles and radicals is of great interest. This program has investigated, through spin-lattice relaxation, the nature of the trapping sites of charged and atomic species. The usual technique involved trapping ions in a solid matrix; the ions themselves were then studied by physical techniques such as paramagnetic resonance, optical spectroscopy, etc.

(U) The paramagnetic relaxation characteristics of trapped electrons and hydrogen atoms in γ-irradiated alkaline, acid and oxyanion ices, and of trapped radicals in methacrylate polymers were studied by power-saturation methods. The relaxation times were measured as a function of radiation dose, deuteration, phase and temperature. Line widths were measured under various conditions. The trapped electron EPR line was found to be inhomogeneously broadened by nuclear hyperfine interactions; the spin-lattice relaxation mechanism a cross-relaxation process with O^{-}; the electrons trapped with a nonuniform spatial distribution in vacancy sites in radiation-produced spurs of 30 Å radius; and the H atoms trapped with spatial uniformity at interstitial sites near oxyanions. The formation of dielectrons in irradiated alkaline ices was demonstrated by high radiation doses and by optical bleaching (dielectrons are diamagnetic and have a broad optical band with a maximum near 900 mμ). The relative reaction rates of mobile electrons in ice were compared with solvated electron rates in water. Mobile and solvated electrons appear to be structurally similar and to react by an electron transfer tunneling mechanism.

(U) Reactions of t-$C_4H_9^+$ in liquid isobutene were also studied. An experimental technique for generating ions in the vapor by photoionization and then injecting them into a liquid with an electric field was developed. Analysis of the resulting C_8 products showed that olefins predominate. Proton transfer is the important termination step for the t-$C_4H_9^+$ reactions but hydride transfer also occurs. Evidence for vibrationally excited t-$C_4H_9^+$ was obtained.

LATEST (FINAL) PUBLICATION:

L. Kevan, J. Zeinbrick, N.S. Viswanathan "Ion Chemistry", AFRPL-TR-67-321, December 1967.

(U) Characterization and Evaluation of Light Metal Hydrides/Lockheed Propulsion Co./Dr. W. Baumgartner/AF 04(611)-11219/Lt W.H. Anders (RPCS)

(C) This contractual effort had two major objectives. The objective of the first phase entailed the detailed characterization and evaluation of various forms of BeH_2 fuel as obtained from different synthesis sources. The evaluation included the formulation, ballistic testing, and shelf-life study of BeH_2 in high-energy solid rocket propellant formulations. The second phase developed methods to measure the diffusivity and solubility of hydrogen gas resulting from AlH_3 decomposition in high-energy propellants.

(C) Phase I efforts resulted in the successful standardization of chemical and physical property determinations for BeH_2. Propellant evaluations utilizing $\frac{1}{4}$-lb and $1\frac{1}{2}$-lb charges proved feasible as manifested by correlation with ballistic results from 20-lb-charge propellants. Delivered BeH_2 motor efficiencies of 95% with I^0_{1000} of 287 seconds were observed in 20-lb-charge propellants. Small formulation studies and motor firings were utilized to evaluate a large variation of BeH_2 propellant parameters. Aging studies established a relatively high thermal stability for BeH_2 propellants (some have withstood 130°F accelerated aging for 1 year without grain failure). Applied combustion studies and computer thermodynamic studies were used to check out candidate BeH_2 propellant systems.

(C) Phase II developed theoretical equations relating gas generation rates, solubility and diffusion coefficients of hydrogen gas in AlH_3 solid propellant formulations. Measurements of these parameters were undertaken to determine failure mechanisms and useful shelf life. Shelf life of AlH_3 propellants can be predicted with only limited accuracy; additional techniques need to be developed to allow predictions within a factor of 2 to 3. A need for AlH_3 of improved thermal stability was

established in that the rate of H_2 generation during the first 0.1% decomposition was shown to be the most critical factor to AlH_3 propellant grain failure.

(C) Effort during this reporting period has been concentrated on the evaluation of dense BeH_2 along with the further study of current batch and continuous process BeH_2 as made by Ethyl Corporation. Effort was also continued to define a quantitative relationship between BeH_2 specific surface area and propellant burning rate. (It was determined that BeH_2 surface area has no major effect on burning rate due to formulation limitations.) Comparisons of new lots of BeH_2 indicate that the very high purity lots were of high quality in terms of propellant compatibility and processability.

(C) Differential scanning calorimetry was employed to establish a qualitative difference in the thermal-decomposition mechanism for light metal hydrides differing in purity. Additional investigation of thermal stability was initiated by thin-layer chromatograph separation of plasticizer decomposition products.

(U) Technical effort was completed in December 1967 and there is no further work on BeH_2 programmed for the near future.

LATEST PUBLICATION:

"Characterization and Evaluation of Light Metal Hydrides", AFRPL-TR-67-243, September 1967, AD 384198.

(U) Kinetics of Decomposition of High-Energy Materials/Lockheed Propulsion Co/Dr. W. Baumgartner/AF 04(611)-11385/Lt R. E. Foscante (RPCS)

(U) The mechanism and kinetics of the thermal decomposition of energetic materials are being examined under conditions simulating adiabatic heating, as would occur at the onset of explosive decomposition and/or during combustion in a solid rocket motor. The experimental conditions for achieving rapid (microseconds) heating of the sample to the desired test temperature have been described in several reports under this contract.

(C) During this reporting period, application of the mass thermal analysis technique to the PBEP (poly 1, 2-bis(difluoroamino)-2, 3-epoxypropane) development problem has continued. The experiments were designed to provide data which would aid in the production of an improved product (higher thermal stability, uniform structure). Specific attention is being given to the identification of species or groups which constitute impurities capable of degrading the material. The mass thermal decomposition data for several pyrolysis runs are being reduced and analyzed. Initial indications from these data are that the observed instability of PBEP may be caused by structural irregularities.

(U) Thermal decomposition studies have recently been initiated on hydrazinium diperchlorate (HP-2). Its pyrolysis history shows initial loss of perchloric acid. Two sequential processes with different activation energies are indicated for this perchloric acid loss. The mass thermal analysis of HP-2 will be pursued actively in the future since it will provide data basic to the understanding of HP-2 stability and combustion behavior.

LATEST PUBLICATION:

"Kinetics of Decomposition of Solid Oxidizers," AFRPL-TR-67-182, June 1967, AD 382753.

(U) The Kinetics of Decomposition of High-Energy Materials/Dow Chemical Co./T. Dergazarian/AF 04(611)-11395/Lt R. E. Foscante (RPCS)

(C) The purpose of the last 9-month phase of the program was to obtain new, basic information on the kinetics and mechanism of decomposition of the energetic prepolymer, poly [1, 2-bis(difluoroamino)-2, 3-epoxypropane] (PBEP). However, before the final objective could be realized, a structural study of several different polymer samples was required to resolve reported inconsistencies in sensitivity and curing properties of the various samples.

(U) The experimental approach for determining the kinetics and mechanism of decomposition of the polymer involved study of the slow isothermal decomposition of PBEP in a platinum and glass reactor system and in a thermal-gravimetric analysis apparatus (TGA). Vapor-phase chromatography (VPC) and mass spectrometry were used routinely as analytical tools.

(C) Nuclear magnetic resonance (NMR), infrared (IR) spectroscopy and elemental analysis were used to determine the structure of the general polymer backbone of as-received PBEP. Of special significance from a stability standpoint, hydrocarbon impurities and the nitrile (CN) group were found present in undecomposed as-received PBEP.

(U) The presence of hydrocarbon impurities in as-received PBEP may have a specific mechanistic effect on the decomposition, and would certainly have an effect on the interpretation of experimental data. For example, a large amount of volatile impurities would have an effect on the initial weight loss and the spattering during pyrolysis. If the spattering effect is assumed to be constant throughout the temperature range of interest, then empirical kinetics may be determined.

(C) Three different molecular weight samples of PBEP were studied in the platinum, cycloidal mass spectrometer system. Analysis of all data supports HF elimination as the most favored step in the decomposition. Regardless of molecular weight, the threshold temperature for HF formation was the same, 77 $\pm 2^{\circ}C$. Residue analysis was, however, very different. These results suggest that an increase in molecular weight has no appreciable effect on thermal stability (relative to HF elimination) but is accompanied by a marked increase in the amount of intractable residue due to cross-linking.

LATEST PUBLICATION:

"Kinetics of Decomposition of Solid Oxidizers," AFRPL-TR-67-265, October 1967, AD 384568.

(U) Engineering Property Data on Rocket Propellants/Rocketdyne/ M. Constantine/AF 04(611)-11407/G. A. Beale (RPCL)

(U) This program involves the analytical and experimental characterization of the physical properties of selected liquid propellants. The program is divided into three phases. Phase I is a literature survey, Phase II is the determination of engineering properties, and Phase III is the compilation of data into handbook form.

(U) The Phase I objective is maintenance of a continuous review of the current literature and efforts of other investigators in the field, to insure acquisition of the latest possible propellant property data for evaluation and possible documentation purposes. This survey is designed to include, but not necessarily be limited to, the following fuels and oxidizers:

OXIDIZERS	FUELS
Liquid Oxygen (LO_2)	Liquid Hydrogen (LH_2)
Chlorine Pentafluoride (ClF_5)	N_2H_4 - UDMH (50-50)
Chlorine Trifluoride (ClF_3)	Hydrazine (N_2H_4)
Fluorine (F_2)	MMH ($CH_3N_2H_3$)
Hydrogen Peroxide (H_2O_2)	UDMH $(CH_3)_2 N_2H_2$
Mixed Oxides of Nitrogen (N_2O_4-NO)	Hybaline B-3
FLOX Mixtures (F_2-O_2)	Alumizine
Oxygen Difluoride (OF_2)	Pentaborane (B_5H_9)
Tetrafluorohydrazine (N_2F_4)	Diborane (B_2H_6)
	MHF Fuels
	MAF Fuels

(U) The literature survey encompasses all reports acquired by the contractor through normal distribution channels. Reports containing potentially useful information are selected for detailed review and collation of pertinent data (to date, 8168 reports have been surveyed

with 751 reports reviewed in detail). This data is then evaluated for authenticity. Valid data is referred to the compilation under Phase III. Invalid or questionable data is held for Phase II consideration.

(U) The objective of Phase II is experimental characterization of the important physical properties of selected propellants. Selection of the propellants and properties to be so characterized is related to the unavailability of required data and relative importance of the data, as determined and periodically reviewed by AFRPL. When practical, the properties of interest are determined over the liquidus temperature range and over a pressure range of 14.7 to 1000 psi. The following list indicates the property data that has been determined under Phase II:

PROPELLANT	PROPERTY	TEMP AND PRESSURE RANGE
ClF_3	Density	-22° to -8°C
	Vapor Pressure	42.9° to 147.6°C
	Sonic Velocity (Compressibility)	(-77° to 69°C) (500 and 1000 psia)
	Surface Tension	0° to 50°C
ClF_5	Sonic Velocity (Compressibility)	(-77° to 69°C) (500 and 1000 psia)
	Inert gas solubility (N_2)	32° and 49°C
	Viscosity	68° and 80°C
	Surface Tension	-51° to -4°C
UDMH	Specific Heat	25° to 70.5°C
	Thermal Conductivity	-18° to 121°C
	Surface Tension	-50° to 50°C
N_2H_4 - UDMH	Specific Heat	2.2° to 49.2°C
MHF-3	Specific Heat	-47.8° to 24.9°C
	Thermal Conductivity	-18° to 121°C
MHF-5	Thermal Conductivity	-18° to 94°C
	Specific Heat	-73° to 70°C
N_2H_4	Surface Tension	10° to 30°C
MMH	Surface Tension	-40° to 60°C

(U) Phase III is concerned with the assembly of all data generated under the other phases, verification of data sources, critical evaluation and comparison of conflicting data, and tabulation and correlation of the results. During the last 12 months, physical property bibliographies were prepared for B_2H_6 and N_2H_4, and data sheets were compiled for N_2H_4. Preparation of a bibliography on N_2O_4 physical properties has also been initiated.

(U) The remaining 3 months of the program will be used to complete the planned property determinations and to undertake additional determinations as requirements arise. At the completion of the program, the compiled data will be presented in a standard format and submitted to the CPIA for inclusion in their propellants handbook.

LATEST PUBLICATION:

AFRPL-TR-67-274, Quarterly Progress Report No. 5, Contract AF 04(611)-11407, October 1967, AD 385671.

OTHER REFERENCES:

AFRPL-TR-67-151, Annual Summary Report, Engineering Property Data on Rocket Propellants, May 1967 (CONFIDENTIAL), AD 382340.

(U) Storable Concentrated Hydrogen Peroxide/Shell Development Co./ Dr. K. D. Detling/AF 04(611)-11416/Lt D. D. Huxtable (RPCL)

(U) The design of systems employing concentrated hydrogen peroxide (H_2O_2) requires allowance in one form or another for the decomposition of a small fraction of the peroxide in the system tanks and lines. For systems intended for long-term storage under sealed conditions, this allowance must be in the form of ullage space and vessel-wall strength in order to confine the gas liberated by decomposition of the peroxide. This investigation is concerned with means of reducing the amount of decomposition of concentrated H_2O_2 which would occur under storage conditions as a result of: dissolved and suspended contaminants in the liquid phase; catalytic activity of the container surfaces submerged in the H_2O_2; and catalytic activity of the container surfaces not submerged but in contact with the vapor from the H_2O_2.

(U) The investigation is addressing methods of purification and stabilization of H_2O_2, also means of preparing and passivating surfaces for contact with H_2O_2. The operational objective of this work is storage of concentrated H_2O_2 in sealed containers for periods up to 5 years.

(U) The most effective ion-exchange bed for purifying H_2O_2 contains B-stannic acid solids as the ion-exchange medium. Water tests showed that flow rates of 100 bed volumes per hour could be obtained. However, upon degradation of B-stannic acid solids on contact with H_2O_2, enough fine particles are formed to cause partial plugging of the exit filler. Two ion-exchange samples stored in Pyrex decomposed at rates less than 0.1% per year while one in Aclar was 0.16% per year.

(U) The stability of the product obtained from redistillation has been satisfactory (decomposition rates on the order of 0.04 to 0.07% per year). The decomposition rate of the product obtained from recrystallization

was approximately 0.10% per year. Samples of HP which have been purified by ion-exchange, distillation, or recrystallization have been placed in Aclar-lined vessels and tin-plated aluminum or steel vessels for storage at 25°C. Two vessels of type 1260 aluminum have been heat-treated with HP in order to reduce their surface activity, and have also been put in storage tests. H_2O_2 samples will be observed for 3 years to determine their decomposition rates.

LATEST PUBLICATION:

AFRPL-TR-67-139, June 1967, AD 815646.

(U) Development and Evaluation of a Hydrocarbon Binder for High-Energy Solid Propellants/Aerojet-General Corporation/Dr. A. J. DiMilo/ AF 04(611)-11419/R. C. Corley (RPCS)

(U) The objective of this program is to further develop and evaluate a solid propellant binder system designed specifically to meet the rigid demands of advanced, high-performance solid rocket motors. The candidate binder system consists of an isocyanate-cured, hydrocarbon prepolymer (Telagen S) developed under Contract AF 04(611)-10386 with Aerojet-General.

(U) The major problem encountered in the application of Telagen S as a binder is the poor low-temperature mechanical properties of the cured system. The present emphasis in this program is directed toward resolution of this problem. To date, the molecular weight of prepolymer has been demonstrated to have no significant effect on low-temperature properties. Dilatometry studies have indicated binder crystallization is not a factor at -10°C. Differential thermal analysis shows characteristic differences between saturated and unsaturated prepolymers. Saturated prepolymers, and the binders made from them, show two generally distinct second-order transitions at about -60° and -40°C. Unsaturated prepolymers and binders show a single second-order transition in the range of -80° to -70°C. A first-order transition, which may be crystallization, was observed in both saturated and unsaturated prepolymers preconditioned at dry-ice temperature for one day. These transitions occurred below -40°C. Because they were also found in unsaturated prepolymers (which generally give good low-temperature properties), these first-order transitions are probably not related to the low-temperature behavior of saturated binders.

(U) The major factor influencing the low-temperature behavior of Telagen S binders and propellants thus appears to be the degree of saturation of the prepolymer. Mixtures of saturated and unsaturated prepolymers give some improvement but not to the same extent as obtained by using partially saturated prepolymers. A comparison of low-temperature properties has shown that a prepolymer of 65% saturation yields results closely approaching those of a standard unsaturated prepolymer. Aging and compatibility studies have been initiated to determine overall improvements available by use of this type prepolymer.

LATEST PUBLICATION:

"The Development and Evaluation of a Hydrocarbon Binder for High-Energy Solid Propellants," AFRPL-TR-67-260, October 1967, AD 820843.

(U) E··aluation of the Combustion of a Light Metal Hydride Gelled Fuel w.·h Selected Oxidizers/Aerojet-General Corp./Dr. S. D. Rosenberg/ A. 04(611)-11535/Capt W. H. Summers (RPCL)

(U) The objective of this program was to determine the effect of fluorine on the combustion and performance efficiency of an oxygen-oxidized beryllium hydride-containing liquid propellant system. Initially, it was planned to attain the objective by evaluation of the combustion characteristics of a mixture of tetranitromethane (TNM), tetrafluorohydrazine (TFH) and the beryllium hydride-containing fuel. This approach, however, was abandoned when a batch of 80/20 wt % TNM/TFH oxidizer blend detonated on being transferred from the oxidizer mix tank to the test facility oxidizer run tank. The objective was finally achieved using a tripropellant injector whose oxidizer circuit contained an injection scheme for both ClF_3 and N_2O_4.

(C) During the test program three beryllium-hydride-containing liquid propellant systems were evaluated in a 1000-lb.-thrust test engine at a chamber pressure of 350 psia. These propellant systems provided the following delivered performance:

SYSTEM	Isp	% THEO	C*	% THEO
TNM/Fuel	228 sec	84	5815 ft/sec	97
N_2O_4/Fuel	245 sec	89	5851 ft/sec	95
N_2O_4 + ClF_3/Fuel	239 sec	87	5787 ft/sec	95

NOTE: The fuel contained the following components: 20% beryllium hydride, 78.9% monomethylhydrazine, 0.8% hydroxyethylcellulose and 0.3% aluminum octoate.

(C) If two-phase nozzle losses are considered, then the test engine delivered 86%, 93% and 90% respectively of specific impulse that was theoretically possible. Thus it is seen that propellant systems containing the high-energy ingredient beryllium hydride can provide good delivered performance.

(U) It was again demonstrated that beryllium propellant systems are temperature-limited and that good combustion efficiencies only occur above a chamber temperature of 2820°K. This was also true for the N_2O_4(80%) + ClF_3(20%) oxidizer tests. It had been hoped that the addition of the halogen species would provide an alternate route in the combustion reaction and eliminate the temperature-limiting process. However, this did not turn out to be the case.

(U) The gelled fuel was subjected to storage stability tests and both bulk growth and gas evolution rates were measured. It was found to have a gel swelling rate of 1.0 vol % per year and a gas evolution rate of 1.3×10^{-5} cc/lb/min. These rates indicate that the fuel is a usable high-energy rocket propellant.

(U) This test program has now been completed; the results will be published in AFRPL-TR-68-7.

(U) High-Energy Plasticizers/Shell Development Company/Dr. K. D. Detling/Subcontractor: United Technology Center/AF 04(611)-11537/ Lt C. S. McDowell (RPCS)

(C) The objective of this effort is to develop a series of energetic NF compounds that can be used effectively as plasticizers in solid difluoramino propellant formulations. These materials will generally consist of carbon "backbones" with suitable pendant combinations of NF_2 and other energetic functional groups, e. g., $-NO_2$ and $-ONO_2$. The new plasticizers developed under this program should substantially improve the ballistic performance and physical property characteristics of the final propellant when compared to similar propellant systems using currently available NF plasticizers.

(C) During the past 6 months the contractor has synthesized two new compounds. The first is a new difluoramino plasticizer: 1, 2, 4, 5-tetrakis (difluoramino) pent-3-yl 2, 3-bis(difluoramino) propylcarbonate (NFAPOC). The other new material is a nitrocellulose plasticizer: 4, 4, 4-trinitrobutylaldehyde cyanohydrin cyanoacetate (TNBCC). Neither of these compounds have been evaluated sufficiently for comment on their util y at this time. Several attempts to synthesize other proposed plasticizers have been unsuccessful.

(C) Substantial progress has been made in scaling-up production of five promising plasticizers synthesized earlier in the program. This involves optimization of reaction conditions, development of techniques for purifying final products and checks on the reproducibility of experimental results. Thus far the following compounds have been synthesized in relatively large lots (100-300g): 2, 3 bis(difluoramino) propyl 4, 4, 4-trinitrobutyrate (NFPTNB); 2, 3 bis(difluoramino) isobutyl 4, 4, 4-trinitrobutyrate (NFIBTNB); 2, 3-bis(difluoramino) propyl 2, 2 dinitropropyl carbonate (NFPODNPOC); di 2, 3-bis(difluoramino) propyl carbonate (BNFPOC); and 2, 2 dinitropropyl α, β - bis(difluoramino) isobutyrate (DNPONFIB).

(C) Currently the most promising candidate plasticizer is NFPODNPOC. This material has demonstrated very satisfactory behavior as a plasticizer for PBEP propellant formulations. The physical properties of NFPODNPOC plasticized PBEP propellants compare favorably with similar PBEP formulations using current NF plasticizers. For example, UTC has reported that the burn rate of NFPODNPOC plasticized PBEP propellant is lower (~1.05 in/sec at 1000 psi) and the pressure burn-rate coefficient is less (n = 0.49) than similar TVOPA-plasticized PBEP propellants (1.25 in/sec at 1000 psi; n = 0.60).

(C) Future work under this contract will involve further evaluation of the plasticizers synthesized to date as well as continued synthesis effort.

LATEST PUBLICATION:

6th Quarterly Report, "High-Energy Plasticizers" (U) Shell Development Company, September 1967.

(U) Optical Spectroscopy Investigation of the Energy-Exchange Process/ University of California, Santa Barbara/Dr. H. P. Broida/AF 04(611)-11538/Dr. L. P. Quinn (RPCL)

(U) The objective of this program is to study a number of collision processes in order to produce information about energy exchange. The major observational technique available for such a purpose is optical spectroscopy. The following areas are being investigated:

a. Mechanisms and cross sections of loss of energy by metastable rare gas atoms and by rare gas ions to produce electronically and vibrationally excited atoms, molecules and ions.

b. Cross sections of charge-exchange collisions resulting in electronically and vibrationally excited products.

c. Dissociation processes induced by photon and electron bombardment leading to rotational and electrical excitation of the products.

d. Charge-transfer processes in electron-donor acceptor complexes in solids at low temperatures.

e. Interactions of rotational, vibrational and electronic energy levels with lattices in rare gas solids.

f. Laser light interactions with phonons in van der Waal liquids and solids.

g. Chemiluminescent reactions of metals in flames and in atomic recombination processes.

h. Kinetics of chemical reactions leading to nonequilibrium and population inversion with emphasis on elucidation of certain laser processes.

(U) The principal accomplishments of these research activities to date have been as follows:

a. Rate coefficients have been measured for thermal-energy reactions of Ar, Kr, N_2, O_2, H_2, NO, CO, and CO_2 with the four long-lived energetic species of helium (the 2 ^3S metastable atom, the a $^3\Sigma$ metastable diatomic molecule, the ground-state atomic ion, and the ground-state molecular ion).

b. Three distinct mechanisms have been found for producing electronically excited CN in mixtures of carbon-containing materials and active nitrogen, and relative rates of formation into the three lowest electronic states have been measured.

c. Absorption measurements of CN in its ground state with concentrations as low as 10^8 molecules/cm^3 have been made in various low-pressure flames.

d. Attempts to observe carbon vapor by absorption spectroscopy in the vacuum ultraviolet region were unsuccessful; this result suggests the possibility of easy aggregate formation from evaporating carbon.

e. A newly developed Zeeman scanning technique was successfully applied to the measurement of absorption-line profiles of atomic metal lines and of two rotational lines of OH in atmospheric and in low-pressure flames.

f. Frequency broadening of light scattered from liquid carbon disulfide has been used to measure viscosity and relaxation times of the attenuation of molecular rotation.

g. Pressure effects on discharge spectra of highly purified helium, oxygen, and nitrogen have been investigated from 0.01 to 100 torr in the spectral range from 1850 to 12,000 Å.

LATEST PUBLICATION:

H. P. Broida, "Quantitative Studies by Optical Spectroscopy of Energy Exchange in Simple Gases and Solids", AFRPL-TR-69-281, October 1967, AD 823877.

(U) Molecular Beam Synthesis/University of Rochester/Dr. D. J. Wilson/ AF 04(611)-11543/Dr. L. P. Quinn (RPCL)

(U) Since most molecular beam experiments involve only very low beam power, it would be of interest to develop techniques for studying selected chemical reactions at beam energies ranging from 10 to 500 electron volts. This should be possible if an ion engine were employed to generate the beam. Use of such a device would allow quantitative determination of the rates of formation and decay of known unstable species, thus providing some of the data required for synthesis and stabilization of energetic species.

(U) The program consists of three phases: construction and "shake-down" of the experimental apparatus, synthesis of energetic species using mono-energetic beams and mass spectral analysis of reaction products, and the theoretical interpretation of experimental results. The high-energy beams will be produced by use of an ion engine. Types of reactions to be studied include rare gas reactions with hydrocarbons.

(U) Construction of the apparatus is complete. Initial tests have shown deficiencies in the butane gun, which are being corrected. No definitive experiments have yet been attempted.

(U) Combustion Study of Light-Metal-Based Fuels/United Technology Center/T. N. Scortia/AF 04(611)-11544/Capt W. H. Summers (RPCL)

(U) In recent years it has become increasingly evident that a better fundamental understanding of the phenomena causing poor performance efficiency is needed before practical propellants using beryllium and beryllium hydride can be formulated. A number of investigations have been conducted to define the parameters which affect performance efficiency in such systems. Although a large amount of empirical information has been generated, there is still need for an understanding of the detailed combustion processes involved, particularly in the case of beryllium hydride. Questions relating to the fuel-phase heterogeneous reactions, the mechanism and sequence of dehydrogenation, and the physical state of the nascent beryllium metal during combustion must be answered before a complete understanding of the combustion of beryllium hydride is achieved. This program was initiated to provide a fundamental understanding of the mechanism involved in the combustion of beryllium hydride under conditions which were free from formulation requirements.

(U) The program has demonstrated that it is feasible to build and operate a high-pressure optical burner for studying the combustion characteristics of various solid materials under controlled rocket chamber conditions. The burner has been used to study the ignition and combustion of aluminum, aluminum hydride and beryllium hydride at a pressure of 300 psia and at temperatures up to 3200°K. The ignition times of all three materials showed a decrease with increasing chamber temperature, as would be expected.

(U) The ignition time of the aluminum hydride is somewhat longer than that measured at atmospheric pressure. This effect, although surprising, may be caused by the absence from the optical burner flame of carbon-containing species which are thought to contribute to the ignition of the

hydrogen evolved from the hydride. The total burning time of the aluminum hydride in the high-pressure burner was shorter than that of aluminum. This effect is opposite to that observed in atmospheric experiments and may be the result of the water-rich atmosphere of the high-pressure burner. However, it is possible that the cooling effect of entrained air in the atmospheric experiments might have caused exaggerated burning times.

(U) The rapid ignition of beryllium hydrides relative to that of aluminum and aluminum hydride in the high-pressure burner, although surprising at first, is in agreement with work conducted at Atlantic Research Corporation. Although the beryllium hydride is injected as single particles in the burner studies rather than as agglomerates as in motor firings, the ignition and combustion details should be the same if the particle sizes are the same. The agglomerate sizes measured in propellant burning experiments are about 50μ and this is the particle size which was used in the burner experiments. Thus, the results of the burner experiments may be considered applicable to motors and suggest that motor combustion efficiency problems are not intrinsic to the combustion of beryllium hydride.

LATEST PUBLICATION:

"Combustion Study of Light-Metal-Based Fuels", AFRPL-TR-67-308, December 1967, AD 386425.

(U) Chemistry of Species in High-Intensity Electrodeless Discharge/
Catholic University of America/Dr. F.X. Powell/AF 04(611)-11546/
Dr. L.P. Quinn (RPCL)

(U) The objective of this program is to study several molecules in an electrodeless discharge in order to discover what species are present, to optimise the conditions for producing these species and to measure their physical properties.

(U) The initial portion of this effort involved construction of an electrodeless discharge unit with its associated pumping and analyzing systems. This was to be followed by a series of experiments designed to evaluate the capabilities of the device and, finally, by examination of a series of free radicals.

(U) The construction phase of the contract has been completed and a series of atoms and free radicals produced to evaluate the apparatus. Nitrogen, hydrogen and oxygen atoms have all been observed. The oxygen atoms have been reacted with other substances such as H_2S to produce OH free radicals. These and other free radicals, including those produced from CH_4 and NH_3, are presently under examination.

LATEST PUBLICATION:

F.X. Powell, AFRPL-TR-67-127, April 1967.

(U) Evaluation of MONEX DW/Rocket Research Corp./Dr. C. D. Good/ AF 04(611)-11549/Capt W. H. Summers (RPCL)

(C) The objective of this program was to evaluate the combustion characteristics of a monopropellant containing beryllium, hydrazine, hydrazine nitrate and water (MONEX DW).* This was accomplished by test firing the gelled monopropellant in a 250-lb-thrust liquid engine.

(C) The results of 32 test firings of the MONEX DW propellant system show that under suitable conditions this propellant will deliver 258 sec of impulse. This is 82.2 percent of impulse theoretically possible at 1935 psia (315 sec) and was achieved on an unoptimized engine system. It was also found during the test program that an excessive amount of slag built up in the engine during each test firing. Thus, if this propellant system is to become useful from an engineering point of view, considerable improvement in the injection scheme is required.

(U) The testing program for this contract has been completed and the final report is being prepared. It is expected that publication and distribution of this report will take place in March of 1968.

*(C) The formulation of MONEX DW 25 6.4-M-1 is:

Beryllium	20.0% by wt
Hydrazine Nitrate	32.3%
Hydrazine	18.8%
Water	23.8%
Teflon	4.7%
Guartee XO-402	0.4%

(U) LMH-1/Hydrazine Heterogeneous Propellant Development/The Dow Chemical Company/Dr. D.A. Rausch/AF 04(611)-11606/R.A. Biggers (RPCL)

(C) Research directed toward the development of a stable, storable, heterogeneous AlH_3 - 1451/N_2H_4 propellant with satisfactory rheological properties is being conducted in an integrated program to furnish a gel system and to study the compatibility of the system components. Phase I, the development and selection of a system, has been completed and a cross-linked polyacrylamide gellant has been selected from four thickening-agent candidates. The selected system is being evaluated and characterized as a part of Phase II. The selection of this polyacrylamide system was based on its superior physical stability characteristics over those of the other candidate systems. The other three systems were: acrylic acid/acrylamide copolymers; ammonium polyacrylates; and the reaction product of oleyl sarcosine and hydrazine (which functions as an emulsifier).

(C) Work is being conducted to determine the chemical nature of the polyacrylamide agent as related to water, hydrazine, and strong bases such as tetramethylguanidine. The effect of aging, at ambient temperature and at 120°F, on the gel physical properties is also being studied. In general, these systems have an evolution rate of about 1.0×10^{-3} cc/lb/min at 77°F and 5.0×10^{-3} cc/lb/min at 120°F.

(C) The effect of the polyacrylamide gelling agent on the stability of AlH_3/N_2H_4 system has been determined. In general, an initial increase of gas evolution was noted in the gelled system versus a reference sample containing no gelling agent. Long-term stability of the gelled sample was at least equivalent to that of the reference sample. The mixing procedure has been modified to low shear mixing, applied intermittently, to counteract the rapid gas evolution experienced with the vigorous stirring

previously used. As a result, gels with excellent physical properties and low gas evolution rates have been prepared; detailed data has not, at this time, been compiled.

(C) Aluminum hydride was found to be stabilized in hydrazine after an initial reaction of the two components. A decelerating rate of gas evolution is established for an indefinite length of time, if the hydride is left in contact with the hydrazine. If the hydride is isolated and reformulated with propellant-grade hydrazine, much less gas is generated initially and the long-term stability persists. The greatest reduction of initial gas evolution was achieved from a prolonged hydrazine pretreatment (6 days) at 60°C. However, equivalent stabilization of the aluminum hydride -1451 has been achieved with n-butylamine and ethyl alcohol in less time than the hydrazine treatment alone. The preceding treatments were successful on only Mg-doped AlH_3; standard AlH_3 (not Mg-doped) does not stabilize with time even when pretreated with hydrazine or other agents.

(C) Efforts are continuing to specify the requirements for scale-up preparation of AlH_3. Mg-doped, diphenylacetylene (DPA)-treated AlH_3 is the most stable type now being produced. The Mg-doping was found to considerably improve long-term stability of AlH_3/N_2H_4 formulations, but DPA may only incrementally improve the stability as it apparently dissolves in the hydrazine.

(U) Work is continuing on the propellant characterization. Physical integrity tests of the heterogeneous gels at 120°F have implied that contaminants from one or several sources may be responsible for gross physical property changes in the gels when they occur. The possible contaminants and their source are now being investigated.

LATEST PUBLICATION:

"LMH-1/Hydrazine Heterogeneous Propellant Development"
AFRPL-TR-67-225, August 1967, AD 383371.

OTHER REFERENCE:

"LMH-1/Hydrazine Heterogeneous Propellant" paper presented by E. T. Niles, 9th Liquid Propulsion Symposium (CPIA), 25-27 October 1967, St. Louis, Missouri.

(U) Synthesis of Rare Gas Compounds/Research Institute of Temple University/Dr. A. D. Kirschenbaum/AF 04(611)-11612/Dr. L. P. Quinn (RPCL)

(U) The objective of this program was to synthesize new rare gas fluorides by various known techniques that have been adapted and redesigned to handle energetic materials. The first compounds to be considered were hypothetical fluorides of argon and neon. Several methods were used in an attempt to prepare ArF_2. Both UV photolysis and spark discharge in the liquid phase produced milligram quantities of a substance whose F/Ar ratio was approximately 2. The substance is not stable, however, and decomposes at temperatures as low as $100^{\circ}K$.

(U) Attempts to make an argon oxide and XeO_3 using liquid irradiation methods were unsuccessful. In view of the instability of the argon fluoride, a portion of the work was redirected to the preparation of other compounds of possible propellant interest which had been postulated in AFRPL-TR-66-228. To this end, premixed N_2 and F_2 as well as Ar and H_2 were passed through a plasma jet. No new compounds were produced by this method, but the spectral lines of metastable NH were seen.

(U) This work has been concluded and the final report will be released in April 1968.

LATEST PUBLICATION:

A. D. Kirschenbaum, Third Quarterly Progress Report on "The Chemistry of Rare Gases", April to June 1967.

OTHER REFERENCE:

S. B. Schneiderman "Theoretical Investigation of High-Energy Metastable Compounds", AFRPL-TR-66-228, September 1966, AD 377319.

(U) Effects of Additives on the Combustion of the N_2O_4/N_2H_4 Propellant System/Dynamic Science Corp./Dr. B. P. Breen/AF 04(611)-11616/ Capt W. H. Summers (RPCL)

(U) Although it is the most energetic member of the family of hydrazine fuels, hydrazine is not currently being used as the sole fuel component in any booster application because of its tendency to produce combustion instability. This phenomenon has caused many test failures in the development of engine systems and a great deal of effort has been expended in describing it analytically. One model of combustion instability (Priem model) has as one of its important parameters the burning rate of the fuel droplet. The model predicts that if the droplet burning rate can be changed, the stability of the engine system can also be changed by a like amount. This, coupled with the fact that hydrazine, because of its monopropellant nature, burns in a two-step decomposition oxidation process, prompted the AFRPL to attempt the stabilization of hydrazine combustion by additives.

(U) A large portion of this program was directed toward determining the burning rate and flame structure of neat hydrazine droplets in order to aid additive selection and comparison of results. It was found that the neat hydrazine burning rate varies linearly with droplet diameter and that a hydrazine decomposition flame exists very close to the droplet surface. This decomposition flame causes a large temperature gradient at the droplet surface resulting in much higher burning rate than found with thermally stable or endothermic decomposing fuels.

(U) Because the hydrazine decomposition flame appeared to be an important factor in the burning rate of the droplet, additives were selected which would modify the hydrazine decomposition kinetics, for example, compounds such as pyridine (hydrogen scavenger) and urea (a NH_2 radical source). Additives were also selected for their role as diluents and thermal modifiers. A complete list of the additives that were evaluated is included as Table I.

(U) It was noted that certain of the additives used during the droplet burning experiments sometimes caused droplet breakup or shattering. This shattering usually led in turn to very rapid combustion of the resulting hydrazine dispersion and therefore offered a great potential for affecting combustion instability. This observation was followed up by purposely adding a liquid explosive, tetranitromethane (TNM), to the hydrazine to cause droplet breakup.

(U) The results of the droplet burning experiments with the TNM hydrazine mixture were quite startling. It was found that these droplets would burn quietly for a short time and then literally explode - producing a burning rate which could not be measured. This effect was still found when as little as 0.25% TNM was added to the hydrazine.

(U) The overall objective of this program was to achieve a modification of the burning rate of hydrazine droplets by chemical means. It was demonstrated that suitable additives can change the quiescent burning rate of hydrazine by as much as 60% and that the burning rate can be either increased or decreased. It was also demonstrated that the use of "shattering agents" can produce extremely rapid hydrazine burning rates. If the Priem Instability Model realistically describes the nature of combustion instability, these results conclusively indicate that rocket combustion may be stabilized with chemical additives.

LATEST PUBLICATION:

AFRPL-TR-67-288, "Effects of Additives on the Combustion of Hydrazine", March 1968.

(U) TABLE I

PROPERTIES OF N_2H_4 BURN RATE ADDITIVES

Additive	Wt %	Formula	Postulated Mechanism	Effect on Burn Rate
Water	10	H_2O	Diluent and Thermal Modifier	Decreased
Hydrazine Nitrate	2	$N_2H_5NO_3$	NO_2 Radical Source	Increased
Fluorobenzene	1	C_6H_5F	H Atom Scavenger	Increased
Pyridine	1	NC_5H_5	H Atom Scavenger	Decreased
Urea	1	$NH_2CO\ NH_2$	NH_2 Radical Source	Increased
Dimethylsulfoxide	1	$(CH_3)_2\ SO$	CH_3 Radical Source	Decreased
Phenylhydrazine	1	$C_6H_5NH.NH_2$	NH, NH_2 Radical Source	Increased
Nitromethane	1	CH_3NO_2	NO_2 Radical Source	Increased
MMH	1,2,10	$CH_3(N_2H_3)$	CH_3 Radical Source and Thermal Modifier	Decreased
UDMH	1,2,5	$(CH_3)_2N_2H_2$	CH_3 Radical Source and Thermal Modifier	Decreased
Tetranitromethane	$\frac{1}{2}, \frac{1}{4}$	$C\ (NO_2)_4$	Shattering Agent	Increased

(U) <u>Methods for Elimination of Corrosion Products of Nitrogen Tetroxide/ Rocketdyne/Dr. E. F. Cain/AF 04(611)-11620/Lt D. D. Huxtable (RPCL)</u>

(U) This contractual effort had two objectives: to study N_2O_4 flow decay as observed under various circumstances and to develop a method of eliminating the corrosion products held responsible for this phenomenon.

(U) N_2O_4 has presented corrosion problems since early space engine test programs when flowmeters often appeared to perform erratically, but upon return for calibration were found to operate satisfactorily without any corrective measures or repairs. In March 1965, a sight-gage valve with a glass port over the needle was observed and photographed under flow-decay conditions. For the first time, a possible cause of the erratic flowmeter behavior had presented itself in visual form as a solid deposit on the needle which caused variations in the flow and eventually complete flow stoppage.

(U) The basic cause of N_2O_4 flow decay has been shown to be gradual deposition of a slightly soluble iron complex, $Fe(NO_3)_3 \cdot N_2O_4$ or $NO^+ [Fe(NO_3)_4]^-$, in small diameter orifices under flow conditions. This metal compound, formed by reaction of the oxidizer with container walls, is soluble in anhydrous N_2O_4 in the range of 1-2 ppm of iron with a slight positive temperature coefficient of solubility. Water at the military specification limit (0.1 weight percent) and NO at the NASA specification limit (< 1.0 weight percent) have no effect on this solubility. Contractor data indicates that flow decay is indeed a solubility phenomenon, with solution, nucleation, and precipitation steps leading to the buildup of deposits. Organic coordinating agents were screened as additives for N_2O_4 under the premise that complexing the iron compound with an organic ligand might alter its solubility and eliminate flow decay; it was found that acetonitrile, benzonitrile, ethyl acetate, and perfluoro-

benzonitrile, at 0.25 w/o concentration were effective additives to this end. Under a follow-on contract with Rocketdyne, methods of eliminating the precipitant and the effects of system variables on precipitation will be further studied.

LATEST PUBLICATION:

AFRPL-TR-67-277, July 1967, AD 823214.

(U) <u>Low-Temperature Synthesis of Fluorine-Containing Species/ University of Tennessee/Dr. G. Mamantov/AF 04(611)-11634/</u> Lt C. S. McDowell (RPCS)

(U) Using a rotating cryostat or low-temperature Andonian dewar in conjunction with various spectroscopic analytical techniques, a study of the generation, stabilization and reactions of fluorine-containing molecular species has been undertaken. The generation of energetic fluorine-containing species at low temperature followed by controlled reaction of these species with other selected materials may lead to the formation of new high-energy oxidizers.

(U) During the current reporting period the contractor has engaged in: the construction of a cryogenic inlet system for a mass spectrometer; Raman spectroscopy studies of liquid FNO; electrospin resonance studies, using new Andonian dewar equipment, on photolyzed ClF_3 or ClF_5 in inert matrices; and infrared studies using new Andonian variable temperature dewar equipment.

(U) No significant chemical results have been realized during this period but considerable progress has been made in improving the analytical methods of studying the generation, stabilization, and reactions of fluorine-containing free radicals.

LATEST PUBLICATION:

1st Quarterly Report, AF 04(611)-11634, "Low-Temperature Synthesis of Fluorine-Containing Species" (U), University of Tennessee, November 1967.

(U) Low-Temperature High-Pressure Study of Hydrogenous Fuels/ Northrop Corp./Dr. K. F. Sterrett/AF 04(611)-11636/Dr. L. P. Quinn (RPCL).

(U) As part of AFRPL's effort to develop synthesis paths to new, dense, and energetic hydrogen-rich fuels, the reactions of PH_3 and NH_3 with hydrogen were examined.

(U) One way of stabilizing the higher hydrides of phosphorus and nitrogen is through increased pressure. Mixtures of their lower hydrides and hydrogen were accordingly subjected to pressures up to 40,000 bars. Phosphorus was examined first since PH_5 has a reasonably good chance of existence inasmuch as phosphorus has available low-lying 3d levels for expanding its coordination shell to five. However, the phosphine-hydrogen studies gave no indications of PH5; hydrogen was produced in situ and was evolved in great excess.

(U) Ten ammonia-hydrogen experiments were performed at pressures of about 10,000 psi in the presence of heated platinum or palladium wires as catalysts. In two of these 10 experiments some unusual behavior of the argon background was observed at M/e ratios of 20 and 40 accompanied by a peak at M/e = 36 which was three times larger than the argon isotope peak normally appearing at this value of M/e (note also that M/e = 36 corresponds to NH_4^{++}). Finally, in two ammonia-hydrogen experiments at 450,000 psi and 200°K and 600,000 psi at 215°K with Raney nickel catalysts, no indications of new species were observed.

LATEST PUBLICATION:

K. F. Sterrett and E. Vigh, AFRPL-TR-67-255, February 1968.

(U) Grain Aging/Aerojet-General Corporation/Dr. A. J. DiMilo/ AF 04(611)-11637/Lt R. W. Bargmeyer (RPCS)

(U) The objectives of this program are to determine the chemistry of the aging process in solid propellants and to correlate observed reactions with changes in propellant ballistics, mechanical properties, and physical properties. The primary analytical techniques being employed are optical microscopy and microanalytical wet chemistry. Propellants being examined include field-aged Hawk motors, Minuteman igniters and Wing I First Stage, Polaris temperature-cycling units, and model motors.

(U) Progress to date includes a thorough mapping of reaction site concentration gradients throughout the various propellant grains being studied. Rate constants and activation energies for the observed reactions have been calculated. It has been shown that the aging reactions can be duplicated in model motors under accelerated aging conditions.

(U) Current effort is directed toward identification of the species present in the observed reaction sites. This task is complicated by the difficulty of obtaining sufficient samples to allow positive identification.

LATEST PUBLICATION:

"Microscopic and Microchemical Study of Aged Solid Propellant Grains", AFRPL-TR-67-289, November 1967, AD 822647.

(U) Study of Stabilization of Hydrogen Atoms at 77°K and Higher Temperatures/United Aircraft Corp./Dr. C. J. Ultee/AF 04(611)-11638/Dr. L. P. Quinn (RPCL)

(U) Because hydrogen atoms contain a large amount of energy/unit weight, they would be of potential propellant interest if large-enough concentrations could be stored. As part of a program to examine materials with this kind of potential, the mechanism of storage of hydrogen atoms in various matrices at 77°K is being determined. Hydrogen atoms can be produced readily by irradiating acidic glasses. Recent reports in the literature have identified certain solid substrates which also can trap hydrogen atoms. Both of these fields are being surveyed to determine which systems will support the highest concentrations. The hydrogen atoms are being produced by irradiation with gamma rays from cobalt 60, detected and measured by electron spin resonance. Warming the sample allows the decay of the hydrogen atoms to be observed, their concentrations measured, the rate constants calculated and finally an activation energy determined.

(U) Among acid systems surveyed the highest concentrations of H atoms can be stored in frozen $HClO_4$. These concentrations of about 10^{19} atoms/cc are stable at 77°K but at higher temperatures there is an initial fast decrease in concentration followed by a much slower decay. These two reactions can be separated by heating the sample until the first decay is complete. Then the second decay can be readily observed. Determining the half-life of the latter reaction at several temperatures allows determination of the activation energy which in this case is 7.7 ± 0.7 kcal/mole. This number probably relates to trapping and diffusion processes and not reactions between H atoms and other species.

(U) Data thus far on solid absorbents indicates that concentrations of hydrogen atoms achievable are a factor of 100 less than in acidic systems.

LATEST PUBLICATION:

C. J. Ultee and C. Kepford, AFRPL-TR-67-143, July 1967, AD 816998.

(U) Energetic Binder Production/Shell Development Co./Dr. K. Detling/ AF 04(611)-11645/Lt W.H. Anders (RPCS)

(C) The objective of this contractual program is development of an efficient method for the continuous production of high-purity poly 1,2-bis(difluoroamino)-2,3 epoxy propane binder (more commonly known as PBEP). PBEP is produced by a three-step process involving polymerization of epichlorohydrin followed by alkaline dehydrochloronation to the unsaturated intermediate, poly (2,3-epoxy propane), and subsequent difluoroamination with N_2F_4 in a continuous flow reactor unit. Total production to date is approximately 65 lbs of PBEP prepolymer.

(C) Major emphasis during this period was placed on scale-up of the continuous-flow difluoroamination reactor unit. Initial feasibility studies were conducted to delineate the optimum production conditions. Production quantities of PBEP were then produced utilizing the continuous-flow reactor. Additional effort was expended in characterization of the product.

(C) PBEP, as currently produced, is a very viscous, yellow-to-amber colored liquid with a number average molecular weight in the range 3500 to 4000. Structurally, the prepolymer is a hydroxyterminated polyether with a nominal functionality of approximately 2. However, this is an average value since the polymer consists of a mixture of trifunctional, difunctional, monofunctional and nonfunctional terminated molecules. The variation in functionality and molecular weight derives largely from the initial polymerization of the precurser (epichlorohydrin). Major problems in thermal stability and curing are believed to be directly related to the low-molecular-weight nonfunctional and monofunctional fractions of the prepolymer.

(C) Future effort, including a 6-month redirection and extension, will concentrate on investigation of the individual steps in the PBEP synthesis to determine conditions and clean-up procedures necessary for producing material of optimum quality. This redirection will include detailed characterization of the current PBEP product via fractionation and gum-stock studies on all resulting samples.

(U) Identification of Exhaust Species from the Combustion of LM and LMH Fuels/Denver Research Institute/W. H. McLain/F04611-67-C-0001/Capt W. H. Summers (RPCL)

(U) The theoretical performance calculations for air-augmented rocket systems are based on the assumption that the solids and combustion gases from the primary rocket chamber will burn with air to form energy-producing oxides. This, however, may not be the case because the fuel-rich combustion of the primary rocket may produce carbides, nitrides, hydrated complexes and complex organic species. If such species survive secondary combustion, the performance of the system will be degraded because of their low energy release. This contractual effort was initiated to determine the nature of the species produced in the fuel-rich combustion of systems containing boron, hydrogen, carbon and oxygen.

(U) Chemical and "real time" spectrographic methods of analysis have been developed and used on this program to provide information concerning the relationships among chemical species formed in fuel-rich boron-containing propellant combinations. An analysis of the chemical composition of the condensed-phase reaction products obtained from an air-augmented, fuel-rich pentaborane-oxygen burner indicated that these products are not simple compounds of boron oxide and boron nitride. Rather it was concluded that a significant fraction of the reaction products was composed of one or more metastable intermediate chemical species which were probably a very complex mixture of boron suboxides and hydrated boron oxides.

(U) The experimental portion of this program has been completed. A detailed account of the experiments and results will be published in the near future.

LATEST PUBLICATION:

AFRPL-TR-67-206, "Identification of Exhaust Species from the Combustion of LM and LMH Fuels", July 1967, AD 818106.

(U) Synthesis of Solid Fluorine Oxidizers/Stanford Research Institute/ M. Hill/F04611-67-C-0002/F. Q. Roberto (RPCS)

(U) The objective of this program was to synthesize new stable and energetic solid oxidizers containing the NF_4^+ specie and to determine their physical properties, compatibility with common propellant constituents, shock sensitivity, and thermal stability.

(C) During the period of this contract, SRI determined the optimum conditions for producing the NF_4^+ cation in the form of an antimonate salt in purity sufficient for use as a reagent in metathetical reactions to form solid oxidizer salts. Two of these salts, NF_4ClO_4 and NF_4HF_2, when projected as solid oxidizers in conventional aluminum composite solid propellants, offer calculated I_{sp} values greater than 300 sec. (1000 → 14.7 psi).

(C) The preparation of NF_4^+ salts was carried out by two general methods. One, direct synthesis reactions of NF_3, F_2 with a series of Lewis acids at high pressures and temperatures, produced the salts: NF_4SbF_6, NF_4AsF_6, NF_4PF_6, and NF_4PtF_6. The failure to synthesis NF_4ClF_6 and NF_4ClF_4 by direct methods confirmed the theory that compounds less acidic than PF_5 (in HF) are not likely to form NF_4^+ salts.

(C) The other method used fully characterized NF_4SbF_6 as a reagent in metathesis reactions. A typical reaction was:

$$NF_4SbF_6 + LiClO_4 \xrightarrow{HF} LiSbF_6 + NF_4ClO_4$$

Similar reactions were used to form NF_4HF_2, NF_4SO_3F, NF_4NO_3, and NF_4BF_4. The perchlorate was found to decompose to NF_3 and $FClO_4$ above -27.5°C; the bifluoride is unstable at -44°C and above; the

fluorosulfonate is unstable at -78°C and above; the nitrate is decomposed in HF solution, but NF_4BF_4 is quite stable (its heat of formation is being determined by the Dow Thermochemical Laboratory). Solvents other than HF were also investigated. Both IF_5 and BrF_5 were found to be an acceptable solvent for NF_4SbF_6. These two solvents will be utilized in future attempts to synthesize NF_4ClF_4 and NF_4BrF_6.

LATEST PUBLICATION:

"Synthesis of Solid Fluorine Oxidizers", Stanford Research Institute, F04611-67-C-0002, Technical Progress Report No. 3, May 1967.

OTHER REFERENCE:

"Synthesis of the Perfluoroammonium Ion, NF_4^+". W. Tolberg et al., Inorg. Chem. 6 1156 (1967).

(U) Research in High-Energy Oxidizers/Rocketdyne/Dr. D. Pilipovich/ F04611-67-C-0007/Dr. F. M. Dewey (RPCS)

(C) Theoretical considerations predict the ONF_2 group to be one of the most energetic yet known, and compounds having this functionality are stable. The objective of this program was to synthesize and characterize new ONF_2 compounds in order that the potential of this promising class of compounds as propellant ingredients might be fully exploited.

(C) A number of compounds were investigated as possible intermediates. Although no new ONF_2-containing materials resulted, an intermediate prepared earlier in the program, potassium difluoramino difluoromethoxide, will be investigated in an electrochemical synthesis approach. Anodic oxidation of this material gave a high yield of tetrafluorohydrazine, indicating the formation of incipient $\cdot NF_2$ radicals. This suggests that utilization of a co-reactant alkoxide would result in formation of the desired product via radical coupling, e.g., $\cdot NF_2 + RO\cdot \longrightarrow RONF_2$.

(U) A follow-on program will investigate electrochemical techniques in the synthesis of these high-energy materials.

LATEST PUBLICATION:

"Research in High-Energy Oxidizers", AFRPL-TR-67-185, June 1967, AD 382456.

(U) Functionality Determination of Binder Prepolymers/Esso Research and Engineering Co./Dr. B. Hudson/F04611-67-C-0012/ Lt R. E. Foscante (RPCS)

(U) The objective of this program is the development of accurate and reasonably fast test methods to determine functionality and molecular weight distribution of the prepolymers currently being developed under Air Force sponsorship.

(U) Methods being investigated and developed for the determination of number average molecular weight ($\overline{M}n$) are vapor pressure osmometry (VPO) and osmodialysis. For the determination of equivalent weight (Eq. Wt.), infrared spectroscopy (IR) and the diborane reaction method are being studied. Molecular weight distribution is being investigated by means of osmodialysis and gel permeation chromatography (GPC).

(U) During this reporting period, functionality distribution measurements based on polymer fractionation by gradient solvent elution from 100 to 200 mesh silica gel show that Telagen-S (hydrogenated hydroxy-terminated polybutadiene) contains about 5 wt.% nonfunctional and 30 wt.% monofunctional components. The reaction of hydroxyl groups with a reactive isocyanate such as toluenesulfonyl isocyanate (TSI) has been used as the basis for a third method for determining the equivalent weight of hydroxy-terminated prepolymers. The reaction is carried out in dilute chloroform solutions and followed by infrared spectroscopy through measurement of the disappearance of the isocyanate group (4.4 to 4.5 microns) as a function of time. The equivalent weight of Telagen-S determined by this method (1090 grams/mole of OH) is in good agreement with previously reported values based on OH absorption intensity (1110 g/mole of OH) and the diborane method (1060 g/mole of OH). In addition, the TSI reaction method was extremely rapid at room temperature (less than 15 minutes for Telagen-S) thereby meeting the rapid-test-procedure requirement.

(This page is Unclassified)

(C) The equivalent weight of PBEP, poly [1,2-bis(difluoroamino)-2,3-epoxypropane], by the TSI method yielded a value of 1770 g/mole OH, which lies between the values obtained by the IR hydroxyl absorption method (2240) and the diborane technique (1300). The functionality of PBEP based on this latest equivalent weight value (1770) and a molecular weight of 3440 is 1.94. This value, since it is based on the isocyanate-hydroxyl reaction, reflects the maximum available functionality of PBEP for the isocyanate curc system.

(U) Fractionation studies of PBEP on silica gel have isolated a major fraction (~ 50%) of high-molecular-weight polymer which has a functionality greater than 2.0. There is evidence of decomposition on the silica gel absorbent, however, which interferes with the intended fractionation by OH functionality.

LATEST PUBLICATION:

"Functionality Determination of Binder Prepolymers", Esso Research and Engineering Co., Contract F04611-67-C-0012, Quarterly Progress Report 4, September 1967, AD 821790.

(U) Radiative Effects on Rocket Stability with Ozone-Containing Oxidizers/General Research Corp./Dr. C.H. Yang/F04611-67-C-0013/Capt W.H. Summers (RPCL)

(U) The objective of this contract was to systematically map the various conditions under which ozone-containing propellants could give rise to local temperature and pressure spikes in an engine environment. The program identified two modes (homogeneous explosion and flame instability) of ozone decomposition which could lead to the destruction of rocket engines using this oxidizer. Also, it was shown that for pure ozone three times as much energy is transmitted upstream by back diffusion of O atoms than is transmitted by conduction down the temperature gradient. In general, this means that pure ozone decomposition flames will accelerate into detonations.

(U) From the mathematical analysis performed during this program the following conclusions about the nature of the ozone system can be drawn:

1. If homogeneous explosions are to be avoided, the flow velocity of ozone must be high enough so that its travel time to the reaction zone is less than 7 μsec.

2. Ozone-oxygen mixtures which contain 25% O_3 or less can be burned stably.

3. Steady-state combustion does not exist for a pure ozone system due to the back diffusion of O atoms.

4. Ozone flames can be stabilized by highly cooled injectors with small-diameter orifices.

5. Additives capable of removing O atoms at temperatures above 1000°K will have significant stabilizing effects on ozone systems.

(This page is Unclassified)

(U) Based on the work conducted under this contract and that under related contracts AF 04(611)-11374 and -11414, it may now be stated that 25% ozone mixtures can be used in an engine system without undue danger of explosions. Also, there is evidence to show that the combustion stability of purer ozone mixtures might be stabilized by the effective use of chemical additives.

LATEST PUBLICATION:

AFRPL-TR-67-296, "Radiative Effects on Rocket Stability with Ozone-Containing Oxidizers", December 1967, AD 824679.

(U) Heat-Transfer Studies of Prepackaged Propellants/Aerojet-General Corp./Dr. N.E. Van Huff/F04611-67-C-0016/Capt W.H. Summers (RPCL)

(U) The objective of this program is to determine the forced convection and critical heat flux characteristics of ClF_5 at subcritical and supercritical pressures. It is being achieved by flowing ClF_5 through electrically heated tubes and determining temperature profiles along the tube's axis.

(U) To make the necessary heat-transfer calculation from the measured temperature profiles, a set of physical properties had to be compiled for ClF_5. This compilation (AFRPL-TR-67-215) provides property values over the range of temperatures from -65°F to +300°F and for pressures up to 5000 psia. It includes experimentally determined values whenever possible; however, the bulk of it was derived from empirical correlations.

(U) A total of 22 heated-tube tests have been completed under this contract. Eight of these tests were conducted at pressures below the critical pressure for ClF_5 (780 psia) while 14 were run at pressures above the critical pressure. The preliminary indications from these tests are that the burnout heat flux for subcritical ClF_5 is comparable to that of other oxidizers (N_2O_4, ClF_3, etc.). The burnout heat flux (ϕ_{BO}) has been found to correlate quite well with the velocity-subcooling product ($V\Delta T$ sub). Thus, the burnout heat flux for subcritical conditions can be predicted quite closely by the equation $\phi_{BO} = 0.00055\ V\Delta T$ sub.

(U) The high-pressure heat-transfer tests demonstrated that ClF_5 can take unusually large heat fluxes before the regenerative cooling system fails. This ability to carry away large amounts of heat is not achieved through an enhancement of the heat-transfer coefficient, but is due mostly to the extremely high wall temperatures (1200°F) which this oxidizer can sustain. Also, testing at supercritical pressures demonstrated that there

is a pronounced pressure effect on the ultimate heat flux. For example, at the same conditions of fluid velocity and bulk temperature, the ultimate heat flux for a pressure of 1000 psia is 10 Btu/in^{2}sec while for a pressure of 3800 it is 30 Btu/m^{2}sec.

(U) Chemical analyses have been run on ClF_5 samples taken from the test system after the sixth heat-transfer test and before and after the extended-duration tests. These anlyses indicate that no significant degradation of the ClF_5 has occurred. Therefore, enhancement of the heat-transfer coefficient through endothermic decomposition of the ClF_5 has probably not occurred.

(U) The only item remaining to be completed on this contract the final heat-transfer data analysis and correlation. It is expected that he results of this program will be published during the first quarter of 1968.

LATEST PUBLICATION:

AFRPL-TR-67-275, "Heat-Transfer Study of Compound A", October 1967, AD 822150.

OTHER REFERENCE:

AFRPL-TR-67-215, "Heat-Transfer Study of Compound A", July 1967, AD 382926.

(U) Applied BeH_2 Combustion/Lockheed Propulsion Co./
Dr. W. Baumgartner/F04611-67-C-0018/Lt W.H. Anders (RPCS)

(C) The objective of this 18-month contractual effort is to achieve a quantitative understanding of the light-metal-hydride combustion process as a basis for attaining high performance in BeH_2 propellants that will also meet tractability requirements for upper-stage rocket motor applications.

(C) A detailed analysis of reported motor-firing data was made in an effort to determine the parameters critical for obtaining efficient combustion in BeH_2-fueled propellants. The main conclusions of this problem-definition task were that the controlling parameters are the binder oxidation ratio and the binder fuel ratio with hydritic hydrogen included. However, a study of CHNO/Be/AP and CHNOF/-BeH_2/AP propellants has indicated that the situation is much more complex than was assumed earlier on the basis of more limited data.

(C) Binder development efforts are now underway to demonstrate that high motor efficiencies can be maintained at high (19 to 20 per cent) BeH_2 loading. The minimal requirements for binder oxidation ratio and binder fuel ratio for high motor efficiencies are 0.8 for the binder oxidation ratio, and 0.5 for the binder fuel ratio at a mass flow rate of 5 pounds per second. Two approaches are currently being pursued. One features the use of solid oxidizer additives such as TNEOC, tetrakis-(trinitroethyl)orthocarbonate, which are at least partially soluble in existing plasticizers and/or exhibit more favorable decomposition kinetics than AP. The other approach involves synthesis of very oxygen-rich plasticizers such as trinitropropyl nitrate (TNPN) or 2, 2-dinitropropanediol dinitrate (DNPDN).

(C) By way of binder evaluation, additional 1.5-lb and 150-gm motors were fired to determine the effect of TNEOC on specific impulse efficiencies. The data show that TNEOC and AP are interchangeable with

no effect on specific impulse efficiencies. A series of 1/4-lb motors plasticized with DNPDN have also been processed for test firing. The propellant was at a 20% BeH_2 loading. At this BeH_2 level the binder fuel ratios approximate closely the values believed critical in obtaining high specific impulse efficiency.

(C) Future effort will obtain ballistic data from micromotor firings of DNPDN plasticized propellants. These firings will take place in closed tanks by groups of 5 to 10 with control charges. The data will be utilized in developing and incorporating binder materials in high-energy BeH_2 propellants which will meet the program targets for performance (I^0_{1000} 295 lbf/lbm) with propellants having tractability characteristics compatible with upper-stage motor requirements (burn rates, thermal stability, mechanical properties).

LATEST PUBLICATION:

"Applied LMH Combustion", AFRPL-TR-67-286, November 1967, AD 385048.

OTHER REFERENCE:

"BeH_2 Propellant Motor Efficiency Analysis", AFRPL-TR-67-183, July 1967, Special Report, AD 384179.

(U) Hydrazine Nitrate Catalyst Development/Shell Development Co./ H. H. Voge/F04611-67-C-0023/G. A. Beale (RPCL)

(C) The purpose of this study is to upgrade the monopropellant hydrazine/ catalyst system by use of higher energy fuels containing hydrazinium nitrate. In most applications this will require a catalyst of greater stability than the present Shell 405 catalyst because of the higher temperatures achievable. The program is designed to obtain a more stable support than the alumina used in 405 and to study better means of incorporating 33% iridium-active material on the substrate. Support stabilities are assessed by surface-area changes on heating in a hydrogen-steam atmosphere at 1100°C. Catalyst stabilities are assessed similarly; and also by operating life, and changes in properties on firing.

(U) Initial work was conducted to determine the stability of candidates for catalyst supports. Thus far, the most stable supports are aluminas modified with 5 to 18% silica. Two other modifiers, zirconia and coprecipitated iridium dioxide, gave some improvement over alumina alone, but both appear inferior to silica.

(U) Shrinkage of 20 cylindrical support pellets before and after heating were measured by calipering. These tests were conducted in small rocket motors and by artificially heating the test specimens. Analysis of this data indicates that the most stable, as judged by retention of surface area and hydrogen chemisorption value after steaming, are those catalysts based on aluminas stabilized with silica.

(C) A number of firing tests were performed under subcontract by Rocket Research Corporation (RRC) in support of this effort. These tests were made with propellant grade hydrazine, and with the 75 w/o N_2H_4 - 24 w/o $N_2H_5NO_3$ - 1 w/o H_2O fuel mixture. The purpose of these tests was to determine whether or not Shell 405 catalyst can be used with the much

hotter burning nitrate fuel and to calibrate the firing reactor for eventual later tests of experimental catalysts supplied by Shell. These tests show good performance with hydrazine, and almost equally good performance with the nitrate fuel. However, measured temperatures with the nitrate fuel indicated that there was an excessive ammonia dissociation level of 75%. Forty-five percent ammonia dissociation is considered desirable for optimum performance. Recently this level has been attained by Shell personnel using a shortened version of their Shell 405 catalyst pack.

(C) A few experimental catalysts based on aluminas stabilized with silica have been tested by RRC with the 75-24-1 nitrate fuel. In these tests ammonia dissociation was as high as 80%, causing poor performance. Otherwise, the catalysts were not degraded.

(U) Future efforts will be made to obtain high performance (low ammonia dissociation) with the hydrazine nitrate fuel by use of a high catalyst bed loading, a short bed, and large catalyst particles of low activity.

LATEST PUBLICATION:

"Hydrazine Nitrate Catalyst Development", Fourth Quarterly Progress Report, December 1967, F04611-67-C-0023, AD 385836.

(U) Thermodynamic Properties of Rocket Propellants and Rocket Exhaust Products (C. C. Selph, RPCL):

(U) Thermodynamic Properties of Rocket Combustion Products/ Philco-Ford Research/Dr. M.H. Boyer/AF 04(611)-11216

Philco-Ford Research/Dr. M.H. Boyer/F04611-68-C-0012

Rocket Power, Inc./M. Farber/F04611-67-C-0010

Space Sciences, Inc./M. Farber/F04611-68-C-0020

(U) Investigation and Compilation of Thermodynamic Properties of Rocket Exhaust/Dow Chemical Co./Dr. D. Stull/F04611-67-C-0009

(U) Investigation of the Thermodynamic Properties and the Decomposition Kinetics of Propellant Ingredients/Dow Chemical Co./Dr. D. Stull/F04611-67-C-0025

(U) The general objective of this area of effort is to determine those properties of rocket propellants and their combustion products which bear on theoretical specific impulse. For propellant ingredients, only the heat of formation is of important concern from a thermodynamic standpoint. For combustion products, entropy and heat capacity are also needed, though heat of formation is again of major importance.

(U) Heats of formation and entropies for combustion products are being derived in this program by a variety of techniques, but most are based on measurement of a high-temperature chemical equilibrium. The most sophisticated of the methods currently under study is the beam-modulation mass-spectrometer combination, which analyses a gaseous mixture by determining the distribution of molecular velocities. Many difficulties have been encountered with this apparatus, but some success has been achieved in the analysis of vapors over lithium fluoride.

(U) Greater success has been obtained with the more conventional approaches such as molecular flow, calorimetry, and ordinary mass spectrometry. Table I shows recent results of these studies. A new

heat of formation of -28.2 kilocalories/mole has also been determined for BeOH $_{(g)}$, which conflicts with an earlier determination of -46.8 kilocalories/mole.

(U) Updating and enlarging of the JANAF Thermochemical Tables has continued with the issuance of Supplements 26 and 27. This compilation now contains tables for nearly 1000 high-temperature species.

(U) Calorimetric methods have yielded new heats of formation for eight propellant ingredients of current interest, as shown in Table II.

(U) Flash-heating studies of the combustion of boron have been completed in atmospheres of O_2, O_2-H_2O, Cl_2, HCl, O_2-F_2, O_2-CH_2F_2, and O_2-CHF_3. The B-NH_4ClO_4 system has also been examined. The most significant findings of these studies are as follows: (1) HOBO is a prominent specie in cases where H and O atoms are present and fluorine is absent; (2) the addition of fluorine (F_2, CH_2F_2, or CHF_3) suppresses HOBO formation; (3) BCl does not appear as a primary intermediate; and (4) BH is an important intermediate in a B-NH_4ClO_4 combination but not in the other cases.

LATEST PUBLICATIONS:

"Investigation of Thermodynamic Properties of Rocket Combustion Products", (Contract AF 04(611)-11216), AFRPL-TR-67-212, September 1967, AD 822492.

"Investigation of the Thermodynamic Properties of Rocket Combustion Products", (Contract F04611-67-C-0010), AFRPL-TR-67-244, August 1967.

"Investigation of the Thermodynamic Properties of Propellant Ingredients and the Burning Mechanisms of Propellants", (Contract F04611-67-C-0025), AFRPL-TR-67-210, July 1967, AD 383031.

TABLE I

(U) HEATS OF FORMATION FOR COMBUSTION PRODUCTS

COMPOUND	$\Delta H_f^o{}_{298}$ (Kcal/mol)
$AlOH(g)$	-42.7
Al_2O (g)	-34.3
* Al_2O_3 (g)	-210
B (g)	138.8
BH (g)	106.7
BO (g)	0.9
* B_2O (g)	17
B_2O_2 (g)	-110.6
CF (g)	61
CF_2 (g)	-39.1
CF_4 (g)	-223.2
ZrCl (g)	37.6
$ZrCl_2$ (g)	-83.3
$ZrCl_3$ (g)	-140.4

TABLE II

(C) HEATS OF FORMATION FOR PROPELLANT INGREDIENTS

CF_3ONF_2	-189.1
$(NH_4)_2N_2H_6(ClO_4)_4$ (DAHTP)	-210
BeH_2 (high-density BeH_2)	-5.0
$Al_9Be_{11}(CH_3)_{29}H_{20}$(ATBH)	-35.7
$C_9H_{14}O_3N_6F_{12}$(TVOPA)	-208.1
CF_3NF_2	-171.7
N_2F_4	-4.8
ClF_3O (Florox)	-35

*Specific Identification Uncertain

(U) Production of LMH-2/Ethyl Corporation/C. Marlett/F04611-67-C-0027/Lt W.H. Anders (RPCS)

(C) The objective of this contractual effort is to supply BeH_2 to the Air Force for use in high-energy propellant characterization and development programs. Additional effort has been directed to improve and further develop the continuous pyrolysis technique for the production of high-purity amorphous BeH_2. Principal emphasis during the report period was on the production of 25 lbs of amorphous LMH-2 and 45 lbs of crystalline LMH-2.

(C) Production of the 45 lbs of dense LMH-2 is proceeding quite smoothly due to perfection of encapsulation techniques on the preceding contractual effort (AF 04(611)-11411, "Research and Development of High Density Crystalline LMH-2"). The posttreatment process utilizes a Harwood Engineering Corporation Hydrostatic Unit with a 2-inch-diameter bore and is capable of producing 1/3 lb of dense LMH-2 per run.

(C) Ethyl Corporation has also reported production of a 7.5-lb batch of BeH_2 with a purity exceeding 98 wt%. This increase in product purity was largely the result of special pilot-plant management and highly skilled plant operators' exercising special effort in process control and contaminant exclusion (previous attempts to produce pilot-plant quantities of high-weight-%-purity BeH_2 have been unsuccessful because of the product's low molecular weight, insolubility and complicated synthesis). About one-third the total production from similar batch pilot-plant operations may be expected to match this purity level.

(C) Future work will concentrate on the production of crystalline LMH-2. This should be completed by February 1968. All production requirements for amorphous BeH_2 have been satisfied and it appears that the specification goals for both the amorphous and dense BeH_2 will be exceeded.

(C) The following table summarizes the results of effort to date on the production of improved grades of BeH_2:

AMORPHOUS LMH-2				DENSE LMH-2	
Component	Goal	Ave	HiPurity	Goal	Ave
BeH_2	92.5 wt%	95.5 wt%	98.4 wt%	90.0 wt%	92.0 wt%
Be Metal	4.0 wt%	1.0 wt%	1.0 wt%	6.0 wt%	1.0 wt%
Be Alkyls	4.5 wt%	2.44 wt%	1.7 wt%	4.5 wt%	2.5 wt%
BeCl	1.0 wt%	0.19 wt%	0.03 wt%	1.0 wt%	0.20 wt%
Be Alkoxides	1.0 wt%	0.04 wt%	0.04 wt%	1.0 wt%	0.10 wt%
True Density	0.62 g/cc	0.64 g/cc	0.65 g/cc	0.75 g/cc	0.77 g/cc
Bulk Density	0.28 g/cc	0.32 g/cc	0.35 g/cc	--	0.60 g/cc
Additives (Li metal)	--	--	--	3.0 wt%	1.5 wt% Li

(U) Detailed information concerning this program will be published in a forthcoming AFRPL Technical Report.

(U) <u>High-Density, High-Temperature Binder/Minnesota Mining and Manufacturing Company/Dr. R. A. Mitsch/F04611-67-C-0030/</u> R. C. Corley (RPCS)

(U) The objective of this program is to provide a binder to fill the needs of air-launched and volume-limited missile systems. The binder must meet the stringent requirements of density and subjected temperature range. To meet this goal, the 3M Company is developing a series of functionally terminated perfluoroalkylene oxide prepolymers. The evaluation of these prepolymers is being accomplished by Hercules, ABL.

(U) The prepolymer which has received the most extensive evaluation to date is prepared by the photopolymerization of perfluorooxydipropionyl fluoride followed by hydrolysis to the carboxyl-terminated derivative. The major deficiencies of this material as a binder are control of pot life (too rapid a cure) and insufficient hydrolytic stability of the cured system. The curing agent currently being evaluated for use with this prepolymer is 2, 6-dioxa-4-spiroheptane (a bisoxetane). This four-membered ring system reacts slower than the conventional epoxides and produces a neopentyl structure which is sufficiently sterically hindered to impart improved hydrolytic stability.

(U) A hydroxyl-terminated prepolymer has been prepared by reduction of the ester derivative. Curing with toluene diisocyanate yields a very tough flexible rubber which has good hydrolytic stability but is not thermally stable over 400°F. A test sample (17 g.) of this prepolymer has been supplied to ABL for evaluation.

(U) Curing of nitrile-terminated prepolymers is also being investigated. These materials, in the presence of tributylantimony oxide, cure to triazine cross-linked rubbers. The cross-link density is adjusted by addition of mononitriles. This cure linkage has excellent thermal and hydrolytic stability. The major problem in this area of work is

synthesizing the nitrile-containing prepolymers. The present method is P_2O_5 dehydration of amide-terminated prepolymers, but this is a difficult, low-yield reaction. Other methods are being sought.

(U) All of the above prepolymers have a 4:1 ratio of CF_2 groups to oxygen atoms in the backbone. Other monomers were investigated to determine the change in polymer properties when the ratio is changed. Table I shows the results and includes POPF polymer properties for comparison.

TABLE I

(U) PHOTOPOLYMERIZATION STUDIES

Run No.	Charge[a]	Moles POAF / Moles PGF	$\overline{M}_n$	f[a]	T_G	TGA 10% Wt. Loss
1	POPF		1900	2.3	-80°F	476°F
2	POAF	1/0	750	2.6	-62°F	404°F
3	POAF & PGF	5/1	1100	3.4	-40°F	441°F
4	"	2/1	1000	2.5	-29°F	437°F
5	"	1/1	1000	2.7	-10°F	446°F

(a) POPF - perfluorooxydipropionyl fluoride
POAF - perfluorooxydiacetyl fluoride
PGF - perfluoroglutaryl fluoride
f - functionality

(U) The major problem in the area of fluorocarbon polymers is synthesis on a large scale. On a laboratory scale, the 3M Company has perfected the photopolymerization technique to reproducibly make polymers having $\overline{M}_n$ of about 2000 with functionalities in the range of 2.2 to 2.5. Three

different types of apparatus are being checked out for pilot-plant use. Pound quantities of polymer should be prepared during early 1968 at which time Hercules, ABL will begin extensive evaluation in propellant formulations.

LATEST PUBLICATION:

"High-Density, High-Temperature Binders", AFRPL-TR-67-316, December 1967.

OTHER REFERENCE:

"High-Density, High-Temperature Binders", Minnesota Mining and Manufacturing Company, Contract No. AF 04(611)-11200, Final Report, AFRPL-TR-67-177, May 1967, AD 383602.

(U) Structure and Reactivity of Chemical Species/University of Kansas/ Dr. L. Kevan/F04611-67-C-0032/Dr. L. P. Quinn (RPCL)

(U) This program is vectored toward a better grasp of the physics and chemistry pertaining to highly energetic chemical species. A balanced experimental and theoretical study of both structure and reactivity of carefully selected species and systems characterizes the approach being used. Specific areas under investigation include: theoretical studies on the structure and stability of H_3^+, CH, C_2 and C_3; development and testing of the theoretical technique of ab initio treatments of large molecules; microwave spectroscopic studies of free radicals, metastable triplets, and vibrationally excited molecules; paramagnetic resonance of radiation-produced transient species; and mobility and recombination of radiation-induced ions in organic solids.

(U) The building blocks of normal chemical bonds are pairs of electrons. Yet modern quantum theory makes extensive use of one-electron orbitals in its attempts to define molecular bonding. This work is using the concept of geminals (two-electron orbitals) to examine the four previously mentioned species. The calculations are ab initio in nature, employing only the Born-Oppenheimer approximations and evaluating all integrals accurately in a nonrelativistic formulation. The basis orbitals for the calculations are Slater-type orbitals and the total wave function is formed using the variation principle and the principles of pair theory, in which the total wave function is expressed as an antisymmetrized product of geminals. Each geminal in this case is composed of a sum of products of natural orbitals which are expressed as linear combinations of basis orbitals. By this approach it should be possible to unambiguously determine whether there are any stable excited states, the correct geometry of such states, etc.

(U) The structural details of excited-state molecules and unstable free radicals have received almost no study by microwave spectroscopy although it is potentially one of the most powerful approaches. After the construction of a sample cell and microwave spectrometer, work under this contract will be aimed at the production of free radicals and other unstable species (such as HNO, NS and PF), and at investigation of their microwave absorption spectra. The unstable species will be produced either directly in the sample cell or pumped in from external reaction chambers.

(U) Hydrocarbons when irradiated with X-rays contain a trapped charge. This charge (both electrons and holes) may be detected by paramagnetic, magnetic and luminescent techniques, and the Hall effect allows determination of the density and sign of the majority charge carriers. Hall measurements and related conductivity studies will be utilized to deduce the hole and electron trap densities and distributions in various types of organic solids. Luminescent techniques will be investigated with respect to energetic recombination reactions of excited transient species produced during irradiation. Paramagnetic resonance will be utilized to characterize the structure and identity of transient radiation-produced species that are present in great enough concentrations.

(U) The nature of the chemical bonding in H_3^+ has been studied by means of a natural-spin orbital analysis of a previously calculated wave function. H_3^+ is shown to resemble closely its united atom analog, Li^+, and the Hartree-Fock energy of H_3^+ is estimated to be -1.301 hartrees. Also, electron-density plots have been developed to clarify the physical picture of the bonding in H_3^+, and suggestions made as to how further calculations might proceed most efficiently. A new method has also been developed for solving the coupled integro-differential equations for determination of the geminals for a system, and geminal theory has been generalized to include odd-electron systems. In the microwave spectrometry area, a

Zeeman modulator and a flow cell have been built for studying transient paramagnetic species. Charge storage in γ-irradiated polymethylmethacrylate (PMMA) at room temperature has been studied by measuring thermoelectric currents. By using pure PMMA as well as PMMA doped with hole and electron traps it has been shown that added electron traps, but not hole traps, lead to charge stabilization. The thermoelectric currents appear to be due to hole mobility. The trapped charge in doped PMMA decays with an activation energy of 0.9 ev. Polyvinyl chloride stabilizes even larger amounts of charge than does doped PMMA.

LATEST PUBLICATION:

L. Kevan, M. Harmony, R. Christoffersen, J. Barnes, AFRPL-TR-67-319, December 1967.

(U) <u>Halogen Passivation Studies/McDonnell Douglas Aircraft Co./</u>
<u>N. A. Tiner/F04611-67-C-0033/Lt D. D. Huxtable (RPCL)</u>

(U) It is frequently assumed that the fluorine passivation process constitutes a final cleaning action in which contaminants which can react with fluorine are removed. The McDonnell Douglas Astropower Laboratory has shown that gross amounts of typical organic impurities are not completely removed by reaction with fluorine at pressures even as high as 200 psig; residues remain that are frequently shock sensitive in liquid fluorine. Considerable evidence has been accumulated to indicate that it is dangerous to assume that passivation processes can be relied upon for final cleaning of systems that have not been properly cleaned before system assembly.

(U) Some of the contract conclusions regarding fluorine passivation are:

1. Exposure of metals to fluorine causes a rapid formation of fluoride films on top of unreacted metal oxide films. The fluoride film is nominally 50Å on top of a 200Å oxide film.

2. Fluoride films are mechanically stable and are not easily removed by flexing or cryogenic thermal shock.

3. Fluoride films are chemically unstable. They are soluble in aqueous HF and cause increased corrosion of substrate metal in aqueous systems. The generation of aqueous HF is made possible by the exposure of fluoride films (which absorb elemental fluorine that is not easily removed) to a warm, humid environment.

4. Hydrated fluorine films can be repassivated, except on copper, by reexposure to fluorine.

5. Fluorine passivation does not remove contamination. Contamination residues after passivation are impact-sensitive and more reactive toward liquid fluorine.

6. Attempts to remove contamination by more strenuous passivation conditions are usually unsuccessful; either removal is still incomplete or the system ignites.

(U) This effort has defined critical areas of fluorine system cleanliness, passivation, and protection. It has also established that, with effective and careful procedures, fluorine can be safely handled and utilized as a rocket propellant.

LATEST PUBLICATION:

AFRPL-TR-67-309, January 1968.

OTHER REFERENCE:

"Halogen Passivation Studies", Douglas Aircraft Co., Final Report, Contract AF 04(611)-10932, AFRPL-TR-66-330, January 1967, AD 805953.

(U) Combustion Mechanism of High-Burning-Rate Solid Propellants/ Thiokol Chemical Corporation/G. F. Mangum/F04611-67-C-0034/ Lt R. W. Bargmeyer (RPCS)

(U) The objective of this program is to develop a capability to tailor the burning rate of a composite solid propellant to any desired level from 1 to 10 inches per second. Ballistic and mechanical properties of the propellants under investigation are to be maintained at the state-of-the-art level of the current Minuteman propellant.

(C) The experimental approach is through continued investigation of the effects of iron compounds on aluminum-ammonium perchlorate-polybutadiene propellants. This class of propellants was intensively studied under a prior AFRPL program at Thiokol, Contract AF 04(611)-11212, the objective of which was to determine how such compounds as iron oxide, ferrocene, and n-butylferrocene function as burn-rate catalysts.

(C) In the present program, many new ferrocene compounds have been synthesized and preliminarily evaluated for melting point, boiling point, and compatibility with oxidizer and binder. Five materials showing excellent promise of substitution for n-butyl ferrocene were selected for scale-up and evaluation in propellant mixes. These compounds are: methoxymethyl ferrocene, allyloxymethyl ferrocene, a 60:40 mixture of 1, 1^1 -di(methoxymethyl) ferrocene and 1-hydroxy methyl - 1^1 - methoxymethyl ferrocene, dimethylaminomethyl ferrocene perchlorate, and bis (α - ferrocenylethyl) ether. They were selected for their wide liquid range, high fuel and iron content, and compatibility with standard propellant ingredients.

(C) During the last year of the program, these materials will be extensively characterized in the Al-AP-PBAN propellant. Their role in combustion will be studied and compared to that of the previously studied catalysts. Finally, a number of advanced propellant ingredients (AlH_3, N-F materials, HAP) will be substituted into the standard propellant to determine their effect on combustion of propellants containing the new catalysts, and how the catalysts influence the combustion of advanced ingredients. Minox propellants will also be briefly examined.

LATEST PBULICATION:

"Combustion Mechanism of High-Burning-Rate Solid Propellants," AFRPL-TR-67-301, December 1967.

REFERENCE PUBLICATION:

"Investigation of the Mechanism of Solid Propellant Burn Rate," AFRPL-TR-67-18, January 1967 (Thiokol Final Report, AF 04(611)-11212), AD 379516.

(U) Study of a High-Energy Fuel/Litton Systems, Inc./Dr. J. Thornton/ F04611-67-C-0037/Dr. L. P. Quinn (RPCL)

(C) Several reports in the classified literature have claimed the storage of energy in discharge-treated hydrocarbons. In this process, a hydrocarbon is evaporated into a helium glow discharge and collected on a cold electrode. Under the discharge action, the hydrocarbon undergoes considerable change into a golden-brown material containing much cross-linking, some double bonds and several types of free radicals. Unfortunately, the process has been characterized by inability to reproduce energetic material, and activation has occurred only randomly. Recent work has attempted to define those parameters that affect the process. Magnetic fields and electrode geometry are two such parameters.

(C) The objective of this program was to determine the reactor geometry and operating conditions that would consistently produce materials with significant energy enhancement. An investigation of reactor geometries which are compatible with increased plasma particle energies was performed. Emphasis was placed on monitoring and controlling the reactor operating conditions and on using various diagnostic tools to determine the state of the plasma discharge. Special attention was also given to the cleanliness of the discharge and to the postdischarge behavior of the treated material.

(C) Work under this contract has been completed and a final report will be released in April 1968. The major results are:

1. No storage of energy was unequivocally demonstrated.

2. Bombardment of the walls of the reactor by secondary electrons released large quantities of undesired material into the reactor. Addition of Helmholtz coils to generate a magnetic field, thus restricting electrons to a path between the two electrodes, reduced outgassing

significantly; application of the magnetic field also increased the density of the discharge. The addition of Meissner coils lowered outgassing further, but samples produced still contained large quantities (up to 20%) of oxygen. The source of the oxygen is not known.

3. Frequent self-ignition of sample materials occurred during pressurization of the calorimeter bomb with oxygen. The cause of this phenomenon is unknown. When the magnetic field and Meissner coils were used, good reproducibility of heat of combustion of the product was achieved.

4. Certain empirical relationships between reactants, products, and discharge current were determined, but could not be related to energy content of the product.

REFERENCE PUBLICATION:

E. A. McLennon, J. A. Thornton, and A. S. Penfold, "Investigations Concerning Energy Storage Using a Low-Pressure Discharge", AFRPL-TR-66-339, January 1967, AD 378599.

(U) Liquid LMH-2 Synthesis and Heterogeneous Fuels Development/ Rocketdyne, A Division of North American Rockwell Corporation/ Dr. E.A. Lawton/F04611-67-C-0038/R.A. Biggers (RPCL)

(U) This program has as its objective the development of beryllium-based liquid fuels with a theoretical specific impulse of 350 seconds or greater when oxidized with H_2O_2 (1000→14.7 psia). The program is divided into four phases:

Phase I: Homogeneous Fuels Synthesis
Phase II: Homogeneous Fuels Characterization
Phase III: Heterogeneous Fuels Formulation
Phase IV: Heterogeneous Fuels Characterization

(C) Phases I and II constitute a continuation of Rocketdyne work performed under Contract AF 04(611)-11532, "Physico-Chemical Characterization of High-Energy Storable Propellants", where it was demonstrated that alane-terminated beryllium hydride (ATBH) liquids could be advantageously used as the fluid media for preparing gelled BeH_2 fuels.

(U) The objective of Phase I is the preparation of homogeneous liquid fuels based on modifications of beryllium hydride. It has been demonstrated that borane-terminated beryllium hydride (BTBH) liquids can be prepared with specific impulses approaching 330 seconds (1000→14.7 psia, H_2O_2 oxidizer). However, despite the attractive aspects of such compounds, no species with a theoretical specific impulse greater than 330 seconds has been prepared and the concept does not appear able to reach the desired specific impulse level.

(C) Several alternate approaches to reach the 340- to 350-second range are now being investigated, namely: liquids containing a central CBe_4 structure; complexes of $(CH_3)_3$ N-BH_3 with beryllium compounds; and reactions of $Be(BH_4)_2$ with allene directed toward producing cyclic

structures. From these three approaches, products have been prepared conforming to: $C(BeH_2BeR)_4$ - where R = alkyl group; $(CH_3)_3$ $N.BH_3$ $(HBeBH_4)$; and solids of low hydridic hydrogen content. The first approach will be continued to strive for a compound of the type $C(BeH_2BeH_2Be-CH_3)_4$ which has a theoretical impulse of 344 seconds (1000⟶14.7 psia, H_2O_2 oxidizer). The second will be further investigated to determine the maximum amount of BeH_2 that can be incorporated in liquid adducts of the type $(CH_3)_3$ $N.BH_3.[(BeH_2)_n BH_4]_2$. The third has been discontinued because solids reach their maximum performance in pure BeH_2.

(C) Stability and flow measurements on heterogeneous BeH_2/ATBH liquids constitute the major portion of work conducted in Phases III and IV. Cab-O-Sil M-5 is a suitable gellant for all the systems under consideration. The gas evolution rate for a typical system of 55 v/o BeH_2/ 45 v/o $(CH_3\ BeH) \cdot (BeH_2)_2 \cdot [Al(CH_3)_3]_2$ is 0.9×10^{-4} cc/lb-min and has remained at this rate for the past 6 months (the theoretical performance of this system is nearly 350 seconds). BeH_2/hydrocarbon mixtures have also been studied because they are of interest in themselves and they approach the 350-second specific impulse goal at approximately 60 w/o loadings. Flow measurements show that a 59 w/o mixture of BeH_2 in dodecane gelled with Cab-O-Sil shear thins as required in the shear range 60 to 1000 reciprocal seconds.

(U) This program is scheduled for completion in July 1968. It will not be extended because of a lack of customer interest in beryllium hydride fuels.

LATEST PUBLICATION:

"Liquid LMH-2 Synthesis and Heterogeneous Fuels Development", AFRPL-TR-67-312, December 1967.

OTHER REFERENCE:

"LMH-2 Fuel Synthesis and Development", paper presented by Dr. L.R. Grant, Propellant Ingredient Synthesis Conference (CPIA), Columbus, Ohio, 3-4 October 1967.

(U) Evaluation of a High-Energy Binder/United Technology Center/ T.N. Scortia/F04611-67-C-0039/Lt W.H. Anders (RPCS)

(C) The objective of this multiphased contractual effort is evaluation of the energetic binder, poly 1,2-bis(difluoroamino) - 2-3 epoxy propane, PBEP. This NF_2-containing polymer, first synthesized by Shell Development Company under AFRPL Contract AF 04(611)-11645, is being evaluated with both advanced and state-of-the-art fuels and oxidizers to determine its compatibility, stability, and sensitivity.

(C). Effort during this period concentrated on establishment of an aging surveillance program. Specimens of PBEP propellant were stored at 25°C (1-lb motors and microtensile specimens) and 35°C (2-inch cubes and microtensile specimens). Thermal-stability studies are being conducted at periodic intervals. This phase of the program involves surveillance of basic formulations containing PBEP from various production lots.

(C) Formulation and compatibility studies are being conducted with HAP, Be metal, and BeH_2 ingredients. Be and BeH_2 show no incompatibility with PBEP-TVOPA by Differential Thermal Analysis tests. However, these fuels must be pacified before mixing, and long-term surveillance will be necessary to determine the stability of their propellant formulations. Cure studies were continued to identify a satisfactory replacement for the HDI (Hexanetriol-diisocyanate) curing agent now utilized with the HAP oxidized TVOPA/PBEP propellant systems.

(U) Binder studies including the fractionation of PBEP were conducted. The fractions were characterized with respect to number average molecular weight and were examined for structural variations by infrared, thermal stability by differential scanning calorimetry, and equivalence by isocyanate gell tests. These studies indicate that PBEP thermal stability problems are related to the high percentage of low-molecular-weight, nonfunctional and monofunctional molecules present in "as-produced" PBEP.

(C) Future efforts will continue the PBEP propellant surveillance studies and expand the compatibility studies to include high-energy ingredients. New PBEP stabilizers and cure agents will undergo screening, and additives producing favorable properties will be incorporated in propellant specimens for long-term storage evaluation.

LATEST PUBLICATION:

"Evaluation of a High-Energy Binder", AFRPL-TR-67-257, August 1967, AD 384754.

(U) Trapping and Spectroscopic Study of Metastable Molecules/ General Electric Company/Dr. M. J. Linevsky/F04611-67-C-0045/ Dr. L. P. Quinn (RPCL)

(U) Theoretical calculations on molecules in the gas phase have shown that certain molecules may exist in metastable states. If such molecules can be obtained in high concentrations they could be of value as rocket propellants. The objective of this program is to determine whether any of these metastable molecules can be isolated. Appropriate reactants are passed through a glow discharge to produce and activate the desired molecules. These are in turn collected in a rare gas matrix (usually neon or argon) which is then examined by emission and/or absorption spectroscopy to see if any of the metastable molecular states have been stored. The gas phase is also examined spectroscopically for the presence of metastables.

(U) After modifications to the apparatus to accept a glow discharge source, NH, HB, AlH, and O_2 have all been examined. No metastable species have been observed in the solid phase. In some cases, large quantities of ground-state material were produced. For example 10^{19} atoms/cc of NH have been observed. In other cases, (BH, AlH), not even ground-state material could be isolated; these molecules apparently undergo recombination before matrix isolation.

(U) Since large quantities of NH could be isolated, an attempt was made to excite ground-state NH to the metastable state with an electron beam. It was unsuccessful.

(U) Present work is concentrated on the $^1\Delta$ state of O_2. This molecule has a long half-life and may be suitable for isolation in an inert matrix. No reports have yet been released on this program.

REFERENCE PUBLICATION:

S. B. Schneiderman, "Theoretical Calculations on Advanced Oxidizers", AFRPL-TR-67-283, November 1967, AD 386005.

(This page is Unclassified)

(U) Combustion Mechanism of Low-Burning-Rate Solid Propellants/ Hercules, Incorporated (Allegany Ballistics Laboratory)/ Dr. R.A. Yount/F04611-67-C-0049/Lt R. W. Bargmeyer (RPCS)

(U) The objective of this program is to develop a capability to tailor, predictably and controllably, the burning rate of composite modified double-base (CMDB) propellants to any desired level in the range 0.1 to 0.3 inches per second, while maintaining performance and physical properties at current standards (using Polaris propellant EJC as a reference).

(U) A comparative approach is being undertaken; that is, the detailed results obtained from relatively idealized experiments on selected samples will be compared with the high-pressure-combustion behavior of identical materials. These fundamental experiments will characterize the dominant chemical reactions and physical factors involved in the condensed-phase and fizz-zone stages of CMDB propellant combustion, and will cover a wide range of samples starting with individual propellant ingredients, progressing systematically to ingredient combinations of increasing complexity and ending with complete CMDB propellants.

(U) During the theoretical portion of the program, a combustion model will be developed, and then tested for validity in a number of small motor firings. The results of motor testing will demonstrate attainment of the practical goal of the program, i.e., the ability to tailor and predict burning rates in the range 0.1 to 0.3 inches per second at reasonable (500 to 700 psia) operating pressures, while maintaining high performance and mechanical properties.

(C) A final phase will be directed toward studies of advanced CMDB propellants containing NF plasticizers as well as advanced oxidizers and fuels.

(U) Effort to date has been primarily concerned with mass spectrometry and differential scanning calorimetry (DSC) of propellant ingredients and ingredient combinations. Appearance potentials for various decomposition species have been measured, and activation energies for the decomposition reactions calculated. Some early conclusions include the following: The type of plasticizer used does not appear to alter the rate-controlling step of decomposition of nitrocelluiose binders at atmospheric pressure. On the basis of heat of explosion versus burning-rate measurements, there appears to be a change in the combustion mechanism of nitrocellulose/nitroglycerin/plasticizer binder systems in the intermediate pressure range (500 to 700 psi). At these pressures, fizz-zone reactions of energetic binder systems are of primary importance in determining burning rate. Incorporating AP or HMX into the binder system also alters the combustion mechanism as evidenced by departures from heat of explosion versus burning rate curves for nitrocellulose/nitroglycerin/triacetin systems.

LATEST PUBLICATION:

"Combustion Mechanism of Low-Burning-Rate Solid Propellants," AFRPL-TR-67-299, October 1967, AD 385913L.

(U) The Development of Low-Temperature Gas Generator Technology/ Rocket Research Corp./Dr. D. Poole/F04611-67-C-0058/ G.A. Beale (RPCL)

(U) This contract continues AFRPL effort to develop low-flame-temperature gas generators for applications such as pressurization, auxiliary power, astronaut maneuvering, expulsion, attitude control, and inflation systems. Its main emphasis is on use of the Shell 405 spontaneous catalyst with hydrazine highly diluted with ammonia and/or water for smooth ignition and steady-state operation as well as clean gaseous exhaust products over a wide temperature range. The present program is being carried out over a period of 12 months and consists of the following 5 phases:

Phase I - Reactor tests to determine the maximum practical concentration of ammonia and water dilutents in the hydrazine-ammonia-water system.

Phase II - Reactor tests to determine the operating characteristics of propellants selected for characterization studies.

Phase III - Materials compatibility studies in order to establish storage properties of the selected propellants.

Phase IV - Physical characterization of the selected propellants as a function of temperature.

Phase V - Development of manufacturing specifications for the selected propellants.

(U) Phase I of the program has been completed. Based on its results, six different propellant compositions were selected for Phase II testing. Exhaust temperatures varied from 475°F to 1100°F. The gas generator

used for these tests operates at a nominal chamber pressure of 300 psia and produces gas at a rate of approximately 60 standard cubic feet per minute. It provided data showing that hydrazine diluted by as much as 70% water is still active with Shell 405 catalyst, although the response is very slow and this mixture is very destructive to the catalyst. A hydrazine content of 45% appears to be the minimum for reliable reactor operation. For propellants containing hydrazine diluted with both ammonia and water, the minimum hydrazine concentration for reactor operation was found to be 42.5%.

(U) The Phase III effort involves compatibility studies of the N_2H_4-NH_3-H_2O propellants with the following metals, welded and unwelded:

Titanium	6 Al-4V
Stainless Steel	347
Stainless Steel	AM 355
Aluminum	6061-T6
Aluminum	1100

The test apparatus consists of two sealed tubes of propellant connected by a differential mercury manometer; one of the tubes contains the metal sample. Any difference in pressure development is observed on the manometer. After 180-day test periods, the metals are examined for weight loss and pitting, and each propellant is analyzed. Preliminary observations indicate that neither type of aluminum is compatible with the N_2H_4-NH_3-H_2O propellants.

(U) The objective of Phase IV was to determine the freezing points, viscosities, densities and vapor pressures as a function of temperature for each propellant of interest. Most of this data is now available.

(U) The experimental portion of the program has been essentially completed. Future effort will include the complete characterization of the referenced six propellant compositions if a requirement arises for their further development; a quality control specification for those propellants of interest will also be written.

REFERENCES:

"The Development of Low-Temperature Gas Generator Technology", October 1967, AFRPL-TR-67-220, AD 819351.

(U) Thermal Stability Surveillance Studies of AlH_3/Dow Chemical Company/Dr. D. A. Rausch/F04611-67-C-0067/Lt R. W. Bargmeyer (RPCS)

(C) The objective of this program is to characterize the long-term thermal stability of various forms of AlH_3. Samples of AlH_3 and propellants containing AlH_3 are being evaluated in a modified Taliani apparatus at temperatures of -15, 25, 40, and 60°C. Materials being investigated include standard undoped macrocrystalline AlH_3 and magnesium-doped AlH_3, as well as samples posttreated with diphenylacetylene. n-butylamine, or water. Various hydride propellants, both composite and double-base type, are on test also. Samples include those produced under previous contracts (AF 04(611)-7554 and -11400) and present production and research efforts (Contracts F04611-68-C-0021 and -0023, AF 04(611)-11461 and F33615-67-C-1619).

(C) Results to date continue to demonstrate an improvement in stability of treated AlH_3 compared to that of standard untreated material. The average decomposition of magnesium-doped samples, containing 0.5 to 0.9 per cent Mg, after 19 months at 25°C is 0.7%. Samples containing 0.9 to 1.4% Mg have decomposed an average 0.06% after 11 months at 25°C; at 40°C about 4.2% decomposition has been observed. Samples which were both Mg-doped and DPA-treated have decomposed about 0.35% after 3 months at 40°C. Original 60°C Taliani data for most of these samples were in the range of 1% decomposition in 11 to 16 days with the best sample having 25 days to 1%.

(C) The stability of AlH_3 in the formulated propellants appears to be improved over that of the neat material with decomposition rates decreasing with time; at 25°C, several samples have gone about 17 months to about .11% decomposition and at 40°C, average decomposition after 17

months is about .5%. However, the validity of this data may be questionable because of small sample size and hydrogen solubility in the binder. A new program at Lockheed Propulsion Company (F04611-68-C-0023) will examine the propellant-shelf-life problem in more detail and attempt to develop improved stabilization techniques.

REFERENCE PUBLICATION:

"High-Energy Propellant Ingredient Research and Development," AFRPL-TR-67-37, January 1967 (Dow Final Report, AF 04(611)-11400), AD 380136.

(U) Catalyst Investigation for 98% Hydrogen Peroxide/FMC Corp./
Dr. L. R. Darbee/F04611-67-C-0068/Lt D. D. Huxtable (RPCL)

(C) The decomposition of 98% H_2O_2 for rocket applications requires catalysts which are both highly active and thermally stable. Complex oxides and metal alloys are being investigated to this end. The complex oxides were formed as pellets and tested with 98% H_2O_2. The maximum temperatures used to prepare the pellets affected their catalytic activity and cohesive strength. By using lower maximum temperatures, the activity of a cobalt metal-manganese oxide pellet developed under the previous contract with FMC was significantly improved. More consistent catalysts with higher activities were obtained by heating the pellets between H_2O_2 decomposition tests, thus simulating a motor restart after previous operation. Pulse-motor tests showed that the pellets are durable enough for motor application, but are in need of greater activity. The effect of an increase in surface area on activity is being determined with crushed oxides.

(C) Granular cobalt metal-manganese oxide has given rapid responses in a 2-pound-thrust motor. This catalyst was also tested in a 40-pound-thrust motor. The ambient temperature start transients were equal to those obtained in the silver-30% palladium catalyst packs. However, the pressure drop across the catalyst packs, and the catalyst and chamber pressures, were too high. A second motor test with cobalt metal-manganese oxide catalyst granules and a minimum of retaining screens will be completed in the near future.

(C) Tests with screen catalysts at regulated temperatures demonstrated a dependence of smooth, rapid-start responses on motor temperature. The alloys containing 10 and 20% palladium in silver exhibited good thermal stability in the operating environment of high-temperature 98% H_2O_2 decomposition gases.

LATEST PUBLICATION:

AFRPL-TR-67-229, August 1967, AD 383149.

OTHER REFERENCES:

"Investigation of Decomposition Catalysts for 98% Hydrogen Peroxide," FMC Final Report, Contract AF 04(611)-11208, AFRPL-TR-67-80, March 1967, AD 380670.

(U) <u>Experimental and Theoretical Investigation of Energetic Compounds for Advanced Chemical Propulsion Systems/United Aircraft Corp./ Dr. C. J. Ultee/F04611-67-C-0069/Dr. L. P. Quinn (RPCL)</u>

(U) Under previous AFRPL contracts, the existence of rare gas oxides and hydrides was predicted by theoretical calculations. The objective of this program is to experimentally establish the existence of these compounds and to define the conditions necessary for their preparation.

(U) The investigation involves the examination of emission spectra of mixtures of oxygen, hydrogen or fluorine with neon, argon, krypton or xenon when excited by various types of discharges. Any band systems which cannot be attributed to the pure components or to accidental impurities will be further examined under high resolution in an attempt to determine their rotational structure and to identify their origin. The choice of gas mixtures will be guided by the results of the theoretical investigations under Contracts AF 04(611)-10380 and AF 04(611)-11214, as well as by information from the literature indicating the existence of new band systems connected with the presence of rare gases.

(U) Results thus far include apparatus construction and a preliminary spectral examination of several systems.

SYSTEM	REMARKS
Xe - O_2	Bands observed
Xe - H_2	No bands observed other than H_2
Ne - O_2	No bands observed
Ne - H_2	No bands observed
Ne - H_2 (at 77°K)	Weak banded emission

LATEST PUBLICATION:

C. J. Ultee, AFRPL-TR-68-10, January 1968.

OTHER REFERENCES:

S. B. Schneiderman, "Theoretical Investigation of High-Energy Metastable Compounds", AFRPL-TR-66-228, September 1966, AD 377319.

(U) High-Temperature Synthesis/FMC Corporation/F. M. West/ F04611-67-C-0070/Dr. F. M. Dewey (RPCS)

(C) Recognizing the potential of ONF_2 compounds as high-energy ingredients for high-performance propellants, their synthesis using high-temperature techniques was undertaken in this program.

(U) This contract was terminated due to a budget cutback. No significant progress was made and no new compounds were prepared.

LATEST PUBLICATION:

"High-Temperature Synthesis," AFRPL-TR-67-237, August 1967, AD 383226.

(U) Double-Base Binder Improvement/Lockheed Propulsion Company/ Dr. G. Meyers/F04611-67-C-0078/Lt W.H. Anders (RPCS)

(U) The objective of this two-year contractual effort is to improve the physical and mechanical properties of composite double-base propellants.

(U) Efforts to date have explored the mechanism of the curing process of both basic manufacturing methods. Difficulty has been experienced in matching the plasticizer levels of the base grain with the slurry-cast systems. It appears that one reason for the generally superior mechanical properties of base-grain propellants may be the necessity for utilization of relatively energetic plasticizers in those systems. Conversely, the poorer performance of slurry-cast systems may result from the necesity for low-energy plasticizers because of pot-life limitations.

(U) The results obtained so far (e.g., failure to obtain satisfactory plasticization in base-grain formulations with slurry-cast ingredients and formulation ratios) support the contention that practical efforts to improve composite modified double-base (CMDB) propellant mechanical properties must emphasize modification or cross-linking of the nitrocellulose (NC) polymer structure. This must be accomplished to achieve favorable solvation characteristics and tractable mechanical properties with the types of high-energy plasticizers that are necessary for ballistic performance.

(U) A majority of the future effort will be concentrated on improving slurry-cast propellants (via cross-linking, chemical and physical modification of NC, and utilization of more favorable plasticizers). Additional work will be done to compare base-grain and slurry-cast propellants via

chemical and mechanical characterization and special effort will focus on characterization of nitrocellulose (e. g., by plasticization and viscosity determinations, supplemented by differential scanning calorimeter (DSC) and infrared analysis).

LATEST PUBLICATION:

AFRPL-TR-67-254, "Double-Base Binder Improvement", September 1967, Quarterly Progress Report, AD 820818.

(U) Critical Review of the Chemistry of Advanced Oxidizers and Fuels/ Midwest Research Institute/Dr. E. W. Lawless/F04611-67-C-0079/ Dr. L. P. Quinn (RPCL)

(U) The original object of this project was accomplishment of an annual review of the latest advances in the chemistry of oxidizers and fuels. These reviews were to be compiled from recent technical reports and the patent literature.

(U) Due to lack of funds this effort has been terminated. The final report covering the first 9 months of work will be released in March 1968.

(U) An Investigation of Reactants for High-Energy Storage/The Marquardt Corp./Dr. R. Kratzer/F04611-67-C-0084/ Dr. L. P. Quinn (RPCL)

(C) Several previous reports from this Laboratory have indicated that energy can be stored in discharge-treated hydrocarbons (see Contract F04611-67-C-0037, this volume). However, the production of such hydrocarbons has been characterized by inability to reproduce activated materials. It was believed that this might be due to insufficient control of parameters or perhaps even lack of knowledge as to which parameters were important. The objective of this contract was to examine the effect on the product of different rare gases, different hydrocarbons, different substrate temperatures, and bound or elemental oxygen.

(C) A large series of experiments were conducted in which these parameters were varied. The products were analyzed by oxygen bomb calorimetry, elemental analysis, electron spin resonance and other techniques, as appropriate. Attempts were made to correlate heat of combustion with the varying parameters.

(C) A total of 57 experiments have been made thus far. No energetic samples have been obtained. The C and H analyses generally totaled $> 98\%$ if the starting material contained double-bonds and $< 95\%$ if the product was prepared from alkanes. While electrode material might conceivably be sputtered into the sample, analyses indicated an insignificant amount of metal present. Data from other contractors suggest that the unidentified material might be oxygen.

(C) Electron spin resonance has shown that in addition to a signal due to hydrocarbon free radicals, there is also a resonance with a g-value between 2.079 and 2.090. There are approximately 10^{20} spins/g contributing to this resonance but its source is unknown.

(C) No evidence has been obtained for the trapping of a rare gas in the product with the exception of xenon. However, the xenon run is anomalous, since the xenon condensed out on the cold electrode.

(U) The final report for this project will be released in April 1968.

REFERENCE PUBLICATION:

R. H. Kratzer and K. L. Paciorek, "An Investigation of High-Energy Storage Concepts", AFRPL-TR-66-236, September 1966, AD 376174L.

(U) Research on Hydrazine Decomposition/Rocketdyne/Dr. A. Axworthy/ F04611-67-C-0087/G. A. Beale (RPCL)

(U) The utility of hydrazine as a storable propellant is well established. Its limitations result principally from a high melting point and limited thermal stability. It is the objective of this program to establish the stability of liquid hydrazine under various conditions and to elucidate its decomposition mechanism. The role of impurities in its decomposition is also being determined.

(U) One of the tasks under this program has investigated the homogeneous decomposition of hydrazine. Ullage, time, surface area and temperature were varied in a series of 17-hour experiments conducted in Pyrex ampoules at 171°C with propellant grade hydrazine. The results, when plotted as percent decomposition against fraction of ullage are independent of the percent ullage, indicating that the observed decomposition occurs in the liquid instead of the gas phase. These pyrolysis experiments give for the first time direct information regarding the thermal stability of liquid hydrazine at elevated temperatures. They also establish the stability of hydrazine vapor under the same conditions (its half-life was estimated to be at least 170 hours). From the test data an activation energy of 22 Kcal/mol was calculated for liquid hydrazine decomposition.

(U) Another series of experiments was conducted at 171°C to determine whether or not the liquid-phase decomposition occurs homogeneously in the bulk of the liquid or heterogeneously on the glass surface of the container. Four pyrex ampoules with their surface areas increased by 2.7 were loaded with propellant-grade hydrazine and heated at 171°C for 1 hour. Control samples without the added surface area underwent 0.062 percent decomposition while each of the ampoules with the added glass area underwent only 0.037 percent decomposition. These results were rechecked and found to be reproducible. The decrease in decomposition with increase in surface area was not expected and is currently under investigation.

(U) A third series of experiments was conducted to determine if the decomposition rate of propellant-grade hydrazine at 171°C varies with the time of heating. It was found that the rate of decomposition decreased with time for approximately 30 hours, after which it appeared to become constant at about 0.013 percent per hour. The rate during the first hour was 0.08 percent per hour; it was then observed to suddenly fall to approximately one-half this rate. Although depletion of a reacting impurity could be a possible cause of this sudden decrease in the decomposition rate, additional tests showed that neither aniline nor water (known impurities) was responsible.

(U) The inorganic impurities in hydrazine were studied by AFRPL as an in-house contribution to the program's objectives. Using emission spectroscopy, atomic absorption, and flame photometry, only chloride and sodium ions were found in significant quantity. Six samples of commercially available hydrazine were analyzed. In addition to the known impurities, (water, aniline and ammonia), 300 ppm toluene was identified. Also a trace quantity of nitrobenzene was determined. Neither of these organic substances contributes to hydrazine instability.

(U) A sample of hydrazine was specially purified by the Olin Mathieson Chemical Corporation for study under this program. The total hydrazine assay after purification was 99.7 percent; the total water content was 0.2 to 0.3 percent; and the estimated ammonia content was 0.1 percent. The aniline content by VPC was found to be 49 ppm by weight. An isothermal chromatogram showed that two carbon-containing trace impurities were present in this purified material; neither was toluene.

(U) Future efforts will extend the investigation of hydrazine decomposition rate as a function of heating time to higher temperatures. The decomposition of hydrazine in various ionic and polar solvents will also be studied as will the effects of water, ammonia and aniline on decomposition rate and on storability when the propellant is in contact with various metal surfaces.

LATEST PUBLICATION:

"Research on Hydrazine Decomposition", AFRPL-TR-67-273, October 1967, AD 823201.

OTHER REFERENCES:

"Characterization of the Inorganic Constituents of Propellant Grade Hydrazine", AFRPL-TM-67-17, July 1967.

(U) Doping Techniques for Light Metal Compounds/IIT Research Institute/ Dr. E.S. Freeman/F04611-67-C-0097/Capt W.H. Summers (RPCL)

(U) The objectives of this program are to determine the mechanisms by which dopants affect the low-temperature ignition of beryllium and beryllium hydride and to develop a doped metal which can be incorporated into a solid or gelled propellant. The first of these objectives will be achieved by studying the nature of low-temperature beryllium ignition with thermogravimetric analysis, differential thermal analysis, and burner techniques. The burner studies will be conducted in such a manner as to permit species determination by spectral and wet chemical analysis. The second objective will be achieved through either liquid media or vapor deposition.

(U) Differential thermal analysis experiments have shown that both beryllium metal and beryllium hydride react directly with some of the dopants. It was also found that several of the doping agents decompose before metal ignition occurs. Therefore, it is likely that the compound which is causing the low-temperature ignition of the beryllium in these cases is not the original doping agent, but one of its decomposition products.

(U) The thermogravimetric experiments have demonstrated that beryllium metal oxidizes very slowly up to a temperature of 800°C. At this point the oxidation rate speeds up but not enough energy is released to cause ignition. However, if $Al_2F_6 \cdot X\ H_2O$ is mixed with the beryllium powder, the low-temperature oxidation is suppressed while the high-temperature reaction becomes explosive and ignition occurs.

(U) Doped beryllium samples have been prepared by dissolving KF in methanol, introducing the beryllium powder to this solution, and then evaporating-off the methanol. Chemical analysis indicates that only 2.2

wt. percent KF is deposited on the beryllium surface by this doping method. There are also indications that the amount of dopant can be decreased by washing in methanol and still produce the desired results.

(U) The beryllium powder doped with KF has been studied in both the Differential Thermal Analyzer (DTA) and the Metal Powder Burner. The DTA studies show that the doped powder reacted violently (exothermally) with oxygen at a temperature of 450°C. This exothermal reaction was taken to indicate both ignition and combustion of the powder. The burner studies also demonstrated that doping enhanced the combustion process. The spectral intensity curves in the flames from the doped and undoped powder show that the doped material burned with 5 to 10 times more intensity than the undoped material.

(U) Inhibited N_2O_4 Engineering Data/Rocketdyne/Dr. K.H. Mueller/ F04611-67-C-0099/Lt D.D. Huxtable (RPCL)

(U) Small amounts of water, picked up during storage, transfer and servicing operations, react with N_2O_4 to form nitric acid. This causes serious compatibility problems since the nitric acid corrodes stainless and aluminum containers, causing leaks and formation of solid residues. The purpose of this program is to reduce the corrosivity of moist N_2O_4 by introducing an additive that will inhibit or prevent the production of HNO_3.

(U) One to three weight percent FNO_2 has been found to effectively reduce the H_2O concentration, thereby acting as an inhibitor. Tests show that FNO_2 is compatible with N_2O_4 and can be easily produced by introducing the proper amount of F_2 into N_2O_4 tanks. Other tests being performed with the inhibited system relate to: solubility, compatibility with construction materials, electrical conductivity, stability, freezing point, transfer effects, analytical techniques, and storability.

(U) The reclamation of wet N_2O_4 as established by a reduction in water equivalency, has been demonstrated by the addition of fluorine. This procedure consisted of bubbling F_2 through liquid N_2O_4 at ambient temperature. However, upon examination of the depleted tanks, it became apparent that the bubbling technique to form FNO_2 in situ caused extensive metal corrosion. Another problem encountered with INTO derives from the high volatility of the FNO_2 inhibitor — large tank storage tests with 3 to 5 weight percent FNO_2 in N_2O_4 at ambient and elevated temperatures demonstrated a depletion to 0% within two months.

(U) The fluorine attack on the metal walls and the high volatility of FNO_2 appear to be major problems which may limit the operational usage of INTO to prepackaged propellant systems when proper passivation can be maintained.

LATEST PUBLICATION:

AFRPL-TR-67-279, "Inhibited N_2O_4 Engineering Data", November 1967, AD 823202.

OTHER REFERENCE:

"Inhibited N_2O_4", Rocketdyne Final Report, Contract AF 04(611)-10809, AFRPL-TR-66-320, January 1967, AD 804976.

(U) High-Temperature Synthesis Study/North American Rockwell Corp., (Rocketdyne)/Dr. H. H. Rogers/F04611-67-C-0104/Dr. L. P. Quinn (RPCL)

(U) Techniques in which the reactants have been raised to high electronic temperatures have been used for the synthesis of several new oxidizers including chlorine pentafluoride. In these techniques, low-pressure glow discharges have been used in which the energy density is relatively low. New energetic oxidizers might be prepared with the aid of a plasma having a higher energy content.

(U) The objective of this study is the modification and use of a high-temperature plasma device to produce new oxidizers. Since the capabilities of such a device are relatively unknown, some time will be spent in evaluation of known systems, such as N_2-O_2, N_2-F_2 and ClF_3-F_2. If it appears that syntheses can be successfully carried out, the preparation of compounds with the general formula $NF_x(OF)_yO_z$ will be attempted. The estimated Isp of such compounds is in the 300- to 350-sec. range. The technique utilized is to select appropriate molecules for reactants (they may or may not be homonuclear); introduce one, or a mixture into the plasma jet; impinge the plasma jet effluent on another reactant (if desired); collect the product and analyze.

(U) In order to characterize the plasma jet the systems N_2-O_2, O_2-F_2, ClF_3-F_2, ClO_2F-F_2 and N_2-F_2 have been examined. Compounds such as NO, ClF, and NF_3 were prepared. Since only relatively simple comounds have been prepared to date, extensive work will be carried out on the nitrogen-fluorine system to see if more selectivity in the synthesis can be obtained before work begins on preparation of new compounds.

(U) An annual summary report on this project will be released in June 1968.

(U) Secondary Combustion of the Pentaborane-Hydrazine System in Air/ Aerojet-General/Dr. S. D. Rosenberg/F04611-67-C-0106/Lt A. W. McPeak (RPCL)

(U) This program is studying the feasibility of secondary combustion, with air, of the primary rocket exhaust of the pentaborane-hydrazine system. Combustion efficiencies and thrust data for the air-augmented system will also be measured.

(U) This primary rocket fuel combination is perhaps unique in that at optimum-thrust operation, as well as fuel-rich operation, 100% of the primary exhaust can be, at least theoretically, further combusted with air. At maximum thrust efficiency the primary system of pentaborane and hydrazine theoretically can deliver 315 seconds of Isp, and 99.5% by volume of the exhaust is hydrogen. The remaining 0.5% is composed of boron and boron nitride with particle sizes in the 0.1 to 1 μ range which will allow very rapid combustion with air if ignition can be achieved. The hydrogen will burn, so if the boron particles do not combust, the system can still achieve 87% theoretical C^*.

(U) Aerojet will use two different liquid micromotor assemblies to gather the required data. The air will be heated to simulated flight air-stagnation temperatures and pressures in an electric resistance tube heater before mixing with the liquid micromotor primary exhaust, and burned in the secondary rocket chamber. Two sets of secondary air conditions will be surveyed, Mach 2.5 on the deck and Mach 4.0 at 40,000 ft. Micromotor A will be a heavily instrumented, water-cooled "work-horse" hardware setup for measuring characteristic velocity (C^*) and exhaust sample collection. The exhaust will be totally collected to determine the extent of combustion versus characteristic velocity measurements. The Micromotor B facility will be designed to measure thrust of the air-augmented system. This motor will be air-cooled, lightly instrumented with no exhaust sampling, but in all other respects, identical with Micromotor A.

The contractor will measure C^* and thrust on the B motor. The C^* measurements will allow comparisons of the data from both micromotors which will tie thrust to the efficiency of the secondary combustion process.

(U) The only test run to date has been with the electric air heater. The goal was 1500°F at 1 lb air/sec. On the first test, with no insulation, 1200°F at 1 lb air/sec was achieved. The additional 300°F should be obtained by preheating the air storage tank and insulating the air lines.

LATEST PUBLICATION:

Second Quarterly Progress Report, AFRPL-TR-67-303, November 1967, AD 823199.

(U) Combustion Species Sampling System/Thiokol Chemical Corp. (RMD)/ T. F. Seamans/F04611-68-C-0007/Capt W. H. Summers (RPCL)

(U) The theoretical evaluation of the performance of any propellant system depends upon assumptions about the chemical species present in the combustion process. It also depends upon the nature of the reactions taking place. Research undertaken at the Air Force Rocket Propulsion Laboratory has shown that in order to understand the reaction mechanisms in the combustion chamber, it is necessary to follow the change in species concentration between the injector face and the chamber throat. The effort under this contract was initiated to develop a system by which gas samples could be taken at various points along the chamber length of the rocket engine which was being fired.

(U) The detailed design of this sampling system has been completed. It consists of a fixed combustion chamber and gas sampling location. Variable sampling is achieved by moving the injector and chamber throat insert back and forth in the tube-like outer chamber. If specie concentration change versus characteristic length is to be studied, the throat insert is fixed in position and just the injector is moved back and forth.

(U) Research on Advanced Oxidizers Having Kinetically Derived Stability/Midwest Research Institute/Dr. E. W. Lawless/F04611-68-C-0010/Lt C.S. McDowell (RPCS)

(C) The objective of this program is the synthesis of new advanced oxidizers possessing kinetically-derived stability. Specifically, MRI has undertaken the synthesis of ClF_6^+ and NF_4^+ salts, ClF_5O, ClF_3O_2 and certain other oxidizer species, the structures of which are analogous to kinetically stabilized molecules such as CF_4, SF_6 and ClO_3F.

(C) Since the initiation of this program in July 1967, the contractor has assembled the necessary equipment and chemicals, and has initiated efforts on the synthesis of ClF_6^+ salts, $NF_4\ NO_2F_2$, $ClO_2\ BiF_6$, $ClF_2\ BiF_6$ and $ClF_4\ BiF_6$. The latter three compounds were prepared for purposes of characterization. An attempt at preparation of $NF_4\ NO_2F_2$, an unknown material, was unsuccessful while reaction of ClF_3, BiF_3 and F_2 at 290°C in a sealed bomb gave a solid material tentatively identified as $ClF_6\ BiF_6$. A similar reaction of ClF_5, AsF_5 and F_2 produced no detectable quantity of $ClF_6\ AsF_6$. Efforts are now being made to identify the material tentatively assigned the structure $ClF_6\ BiF_6$.

LATEST PUBLICATION:

1st Quarterly Report, F04611-68-C-0010, (U) "Research on Advanced Oxidizers Having Kinetically Derived Stability", Midwest Research Institute, Project No. 3099-C, October 1967, AD 384939.

(U) Stability and Compatibility Studies on Advanced Rocket Propellant Components/Midwest Research Institute/Dr. I. Smith/AF04611-68-C-0011/Lt R. E. Foscante (RPCS)

(C) The general program objectives are to evaluate advanced propellant ingredients in terms of oxidizer-binder compatibility, oxidizer stability, propellant stability and processing parameters. The current effort entails an evaluation of stabilities of hydroxylammonium perchlorate (HAP) and hydrazinium diperchlorate (HP-2) as solid propellant oxidizers, and poly [1, 2-bis(difluoroamino)-2, 3-epoxypropane] (PBEP) as an energetic binder. The approach is to identify fundamentally important reactions which occur during the decomposition of the individual propellant components and the reactions which occur between these ingredients. Hence, the program will address the following propellant stability parameters: (1) temperature limits for propellant processing, (2) identification of the least stable and least compatible propellant component before and after curing, and (3) prediction of long-term propellant storability.

(U) The test conditions employed are those which most closely approximate actual processing and storage environments. Experimental techniques used in this study include infrared, nuclear magnetic resonance, and electron spin resonance spectroscopies, mass spectrometry, gas chromatography, and wet chemical methods.

(C) Highlights of the PBEP stability studies to date include an examination of its decomposition products and rates over a temperature range from ambient to 150°C. The initial gaseous decomposition product observed at the test temperatures (and the only product at 80°C) is HF. At temperatures of 100°C and greater, significant amounts of HNF_2, HCN, and N_2O are found in the gas phase in addition to HF. In addition, considerable amounts of impurities (usually residual solvent from the production process) were found in as-received samples of PBEP.

(C) An evaluation of the thermal and reactive stability of the PBEP/HAP and PBEP/HP-2 systems has begun. In the former (PBEP/HAP only) compatibility is observed at 25°C for one day but reactions occur at higher temperatures such as 60 and 85°C. Ultimately, the entire PBEP-advanced perchlorate oxidizer propellant system will be evaluated relative to its thermal and reactive stability.

(U) Screening of the compatibility of HAP and HP-2 with propellant components and functionalitites has been completed and reported under a previous contract with MRI. One of the objectives of the current program is to extend that HAP and HP-2 evaluation to actual binders and propellants so that the overall utility of these oxidizers can be determined.

LATEST PUBLICATION:

"Studies of Stability Problems in Advanced Propellants", Midwest Research Institute, Contract F04611-67-C-0022, Final Report, AFRPL-TR-67-304, December 1967.

(U) Thermal Stability and Kinetic Studies of AlH_3/Dow Chemical Company/ Dr. D.A. Rausch/F04611-68-C-0021 Lt R.W. Bargmeyer (RPCS)

(C) Under a previous program at Lockheed Propulsion Company, it was found that the rate of gassing of AlH_3 during its first several tenths of one per cent total decomposition was sufficiently high to cause failure of a propellant grain more than a few centimeters in thickness. New programs have been started at Lockheed and at Dow Chemical Company directed at improving the long-term thermal stability of AlH_3 and at developing techniques to stabilize the AlH_3 within the propellant and lengthen the propellant shelf life.

(C) The specific objectives of the Dow program are: to determine the chemical kinetics and mechanism of AlH_3 thermal decomposition as well as the role of stabilization techniques in retarding decomposition; and to apply this acquired knowledge to the AlH_3 manufacturing process so as to produce a product with thermal stability sufficient to allow its incorporation into advanced solid propellant motors.

(C) The program began on 1 November 1967 and will run for 2 years. Effort initiated during the first 2 months has been directed toward a thorough analytical characterization of the AlH_3—surface characteristics, bulk properties, internal crystal structure, etc. Various techniques to dope the AlH_3 or posttreat it via a wash will be thoroughly investigated. Results of Dow's efforts are being closely checked by Lockheed, and any resulting improved form of AlH_3 will be evaluated by Lockheed. Techniques of synthesis which yield improvements in thermal stability will be evaluated for inclusion in the manufacturing process under an Air Force Materials Laboratory program with Dow under Contract F33615-67-C-1619.

REFERENCE PUBLICATIONS:

"Characterization and Evaluation of Light Metal Hydrides," AFRPL-TR-67-61, February 1967 (Lockheed Propulsion Company 5th Quarterly Report, AF 04(611)-11219), AD 380340.

"High-Energy Propellant Ingredient Research and Development," AFRPL-TR-67-37, January 1967 (Dow Final Report, AF 04(611)-11400), AD 380136.

(U) Analysis and Improvement of AlH_3 Propellant Shelf Life/Lockheed Propulsion Company/Dr. W. E. Baumgartner/F04611-68-C-0023/ Lt R. W. Bargmeyer (RPCS)

(C) Under a previous program at Lockheed Propulsion Company (Contract AF 04(611)-11219) it was found that the decomposition of AlH_3 within a propellant would cause the grain to fail (by cracking, swelling, or microporosity) after only several tenths of one percent decomposition had occurred. This program was instituted to examine the shelf-life problem in more detail and to find techniques to stabilize AlH_3 within the propellant grain. Its specific objectives are: (1) to be able to definitively predict AlH_3 propellant shelf life in any size or configuration motor based on a knowledge of preformulation AlH_3 thermal stability data and propellant mechanical properties; and (2) to demonstrate practical means of extending AlH_3 propellant shelf life to such time periods as would allow its use in a future weapons system.

(C) The program began 15 November 1967 and will run for 2 years with long-term propellant surveillance extending for an additional year. Effort during the first 2 months has been confined to analytical methods development and evaluation, and model propellant system development. The propellant system of interest is composed of the high-energy fuel AlH_3, difluoramino binder, and an advanced oxidizer. Early experiments will be performed in a polyurethane binder with ammonium perchlorate oxidizer while development effort on the advanced propellant is completed.

(C) This program addresses the most critical problem in the development of an AlH_3 propellant. It is expected to determine, by the end of 1968, if AlH_3 can be stabilized to the extent necessary for its incorporation into a large solid motor with a shelf life adequate for operational purposes.

REFERENCE PUBLICATION:

"Characterization and Evaluation of Light Metal Hydrides," AFRPL-TR-67-61, February 1967 (Lockheed 5th Quarterly Report, AF 04(611)-11219) AD 380340.

(U) Kinetics and Mechanism of Photochemical Decomposition of Ozone by Ultraviolet Light/Universidad Nacional de La Plata/Dr. H. J. Schumacher/AF-AFOSR-979-65/Lt D. D. Huxtable (RPCL)

(U) The objective of this contractual effort was to establish the possible routes of decomposition of ozone in order to better define its stability. The specific areas investigated were as follows: the photochemical decomposition of ozone by use of an Hg-line 313-mu light source; the behavior of O (^{1}D) atoms as species possibly capable of initiating ozone decomposition; the kinetics of the O (^{1}D) + O_3 going to 2 O_2 in the presence of oxygen and inert gases; and the reaction between normal and excited oxygen atoms with carbon monoxide.

(U) This contract has been completed and publication of the final report is pending.

(U) Thermodynamic and Transport Properties of Liquid Fluorine/ National Bureau of Standards, Cryogenic Engineering Laboratories/ D. E. Diller/Contract MIPR-AFRPL 7-3/R. A. Biggers (RPCL)

(U) This is a 4-year effort to obtain precise engineering data on the properties of liquid fluorine over wide temperature and pressure ranges. Currently, NBS is preparing its facilities and measuring equipment for fluorine service.

(U) NBS will determine the following properties of liquid fluorine:

a. Pressure-Volume-Temperature behavior (including vapor pressure and densities of saturated liquid and vapor) to an accuracy of 0.05%.

b. Specific heat at constant volume to an accuracy of 0.5%.

c. Velocity of sound to an accuracy of 0.05%.

d. Dielectric constant to an accuracy of 0.05%.

e. Viscosity to an accuracy of 0.5%.

f. Thermal conductivity to an accuracy of 1%.

The measurements will be made within the termperature range of 53.3°K to 300°K and within the pressure range of 0 to 3000 psi.

(U) The resulting data will be used to derive the following thermodynamic functions: specific heat at constant pressure; enthalpy; entropy; internal energy; compressibility; thermal expansion coefficient; and latent heat of vaporization.

(U) It is assumed that the data produced will be of such accuracy as to be recognized as definitive or standard for all presently foreseeable low-temperature engineering calculations on fluorine. All measured and calculated data will be published and distributed in handbook form.

IN-HOUSE LABORATORY PROGRAM

(U) Propellant Synthesis/Project 314801ACL/Dr. C.I. Merrill (RPCC)

(U) This project has a dual objective: to prepare new compounds of potential interest as propellant ingredients and to synthesize state-of-the-art ingredients by new processes that should bring about a significant increase in their availability and/or a sizable reduction in their cost. When preparing new propellant materials, the intent is generally to achieve one or more of the following goals: higher energy content; improved thermal stability; better chemical compatibility; higher density; and special performance characteristics such as faster burning rates for solid propellants. The project is concerned with both liquid and solid propellant, but primary emphasis is on the latter.

(C) Progress during the past 6 months includes the following significant accomplishments:

1. Methoxyamine perchlorate has been prepared as a model compound and for evaluation as a possible propellant additive to certain systems. Its physical properties, which are still under investigation, should aid in determining the suitability of analogous materials as propellant ingredients.

2. Preparation of 4-ferrocenyl-2-methyl-1-epoxybutane seems to have been attained although characterization of the material is still in progress. This compound may find use as a burning-rate accelerator.

3. A process for quantitative generation of nitrogen trifluoride has been developed. This is a possible propellant material and also an important precursor for difluoramino propellants.

4. A process has been worked out for the preparation of ultra-high-purity fluorines as required for certain sythesis reactions.

(C) Attempts to synthesize oxydifluoramino substances or multifunctional oxyamine perchlorates have been unsuccessful. Effort in this area will be continued until all logical approaches have been exhausted or success achieved.

(C) Activities for the immediate future will largely concentrate on the synthesis of oxydifluoramine substances by direct fluorination of oxyamines; the preparation of oxyamine perchlorate salts (for evaluation as oxygen oxidizers) using displacement reactions to form intermediates; and the preparation of ferrocenyl epoxides (of potential interest as burning-rate accelerators).

IN-HOUSE LABORATORY PROGRAM

(U) Propellant Specification Development/314802ACE/L. A. Dee (RPCCA)

(U) The continuing general objective of this project is to re-view and update or develop suitable standard, analytical methods, and sampling procedures for the quality control of liquid rocket propellants. Analytical techniques and advanced concepts appearing in the current literature are studied and adapted for use. If required techniques are not available, they are developed by the application of modern chemical technology to the specific problems at hand. The developed and evaluated techniques are then incorporated into specifications and technical orders as appropriate.

(U) Analytical methods have been evaluated or developed for the following propellants: N_2O_4, $\frac{1}{2}$% NO/N_2O_4, MMH, BA1014 ($MMH/H_2O/N_2H_4$) and IRFNA. Procurement specifications have also been generated for these propellants.

(U) Future work will be directed toward improved test methods for propellants difficult to analyze, such as ClF_3, ClF_5, F_2 and N_2O_4.

PUBLICATIONS:

"Characteristics of the Inorganic Constituents in Propellant Grade Hydrazine" - AFRPL-TM-67-17, July 1967.

"Gas Chromatographic Separation of Hydrazine Mixtures and Water" - Anal. Chem., 39, 1165 (1967).

"Propellant Specifications, Preparation and Use", Forbes S. Forbes, AFRPL-TR-67-256, October 1967.

(U) Development and Exploratory Evaluation of Heterogeneous Propellants/ Project 314802ICH/G. E. Shoemaker (RPCE)

(U) The AFRPL has been actively engaged in gelled and emulsified fuel development for several years. Laboratory and thrust engine facilities for evaluating heterogeneous fuels are operational. Engine hardware modifications are presently being performed to permit testing of toxic propellants.

(U) Equipment available for gel characterization includes a capillary viscometer (ASTM-D1092), a rising sphere rheometer, penetrometer (ASTM D217), mixers, dry boxes and constant-temperature baths. In recent months, an all-glass apparatus was fabricated for gas evolution studies of candidate gel systems under controlled-temperature conditions.

(U) Investigations during this reporting period have been almost exclusively devoted to the production and characterization of hydrazine gels containing aluminum. A 1-pound air-driven mixer equipped with an anchor-type stirrer was used to formulate 100- to 500-gm batches of alumizine gel for evaluation purposes; batch-to-batch variation was minimized and good agreement achieved between these production batches and small-scale laboratory preparations. Another activity involved the spatula mixing of 100-gm batches of aluminum hydride-hydrazine gels in a dry box for compatibility studies with various gelling agents. Initial testing seemed to indicate that acceptable gels could be formulated. However, outgassing and resultant void formation occurred after a few days at room temperature. Work on this system has been discontinued. A series of 100-pound-thrust engine tests are being conducted with alumizine fuel against N_2O_4 to establish a baseline for testing of other slurried or gelled fuels.

(U) Advanced boron slurry propellants, with improved ignition characteristics have recently become of interest as potential air-augmented rocket fuels. Laboratory characterization of MARNAF 731, a hydrocarbon-boron slurry developed by the Marquardt Corporation, has been initiated. Viscosity data at 77°F (25°C) is being obtained with the ASTM-D1092 capillary viscometer. Firing tests of this fuel (with halogenated oxidizers) will commence after baseline engine tests have been completed. Due to the high vapor pressure of TMH (trimethylhexane), used as a carrier in MARNAF 731, care must be exercised during loading and testing operations to prevent drying of the material. Low-temperature viscosity data and shelf-life studies under controlled temperature conditions will probably conclude the AFRPL evaluation of this boron-slurry system. Future work on boron-slurry systems will focus on hydrocarbon-pentaborane carriers. Increased performance in hydrocarbon or hydrocarbon-pentaborane carriers may be achieved by the addition of high-purity boron. Surface-active agents will also be screened to determine their effect upon increased solids loading.

IN-HOUSE LABORATORY PROGRAM

(U) Inhibited Nitrogen Tetroxide Evaluation (INTO)/Project 314803ACI/
Lt L.P. Barclay (RPCE)

(U) Nitrogen tetroxide (NTO) normally contains a certain amount of water. The controlling military specification permits a maximum of 0.2%; however, the propellant tends to pick up more during handling. The water reacts with the NTO to form nitric acid which in turn attacks the metal tankage; the nature of this corrosion reaction is such that all the original water is regenerated and thus the acid is never used up. It has been found that fluorine will react with NTO to form a compound that will break the acid cycle by removing the water. This compound, FNO_2, has a high vapor pressure and an unfavorable heat of formation (however, the most comprehensive study of FNO_2 was made in the early 1930's and much of the data is disputable). An extensive study of FNO_2-NTO solutions is being made under contract with Rocketdyne (F04611-67-C-0099).

(U) In the meantime, NTO storage containers have failed under field usage and the corrosion problem is receiving much attention from many agencies. Although the in situ formation or addition of FNO_2 to form inhibited nitrogen tetroxide (INTO) does constitute a fix for the corrosion problem, the effects of FNO_2 on the performance of NTO as a propellant oxidizer are unknown. It is the objective of this project to determine their effects.

(U) To date, firing tests have been conducted with hydrazine, "50/50" and MHF-3 with both NTO and INTO. Results were not conclusive, however, and further firings as well as additional data analysis are indicated. It has tentatively been concluded that inhibited nitrogen tetroxide delivers a slightly lower specific impulse with hydrazine and MHF-3 than neat NTO. It follows that the latter would normally be preferred for use in primary propulsion systems. In the case of small space storable propulsion systems where specific impulse is a minor factor, INTO could prove advantageous.

(U) Propellant Kinetics/Project 314803BCB/Dr. W.C. Solomon (RPCC)

(U) The continuing objective of this project is to obtain kinetic and mechanistic data suitable for application to rocket propulsion problems concerning ignition, nonequilibrium combustion, chemical stability and additives.

(U) Static, flow, and shock-tube reactor systems are being used to cover a broad range of pressure and temperature regimes for propellants of interest. Available detection techniques include mass spectrometers and spectrophotometers. Propellants under study include fluorine-hydrogen, interhalogen oxidizers, hydrazine, and oxygen difluoride. Improved calculation procedures, both analog and digital, are being developed and their utility assessed.

(U) Major advances have been made in the area of calculation procedures. A technique has been established whereby an isothermal chemical reaction may be simulated by an analog computer. This allows the researcher to vary rate parameters and reaction conditions to provide a direct solution to the differential equations describing the reaction. Such solutions would be difficult, if not impossible, on digital computers.

(U) Analog simulation technique was used in determining the decomposition kinetics of oxygen difluoride. It provided data which is also being used in interpretation of the oxygen difluoride-hydrogen and the oxygen-inhibited hydrogen-fluorine systems. Calculations have shown an excellent correlation between nonequilibrium kinetic computed values and actual engine performance data in describing the specific impulse of the hydrogen-fluorine propellant system. This illustrates the need for kinetic studies of proposed propellant systems in order to calculate their true potential as opposed to their thermodynamic theoretical potential and to obtain an insight into ignition phenomena and nonequilibrium flow problems.

PUBLICATIONS:

J. Blauer, "Kinetics of Dissociation of HF Behind Incident Shock Waves", AFRPL-TR-67-66, June 1967, AD 651225.

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(U) Propellant Thermochemistry and Combustion/Project 314803BCF/ Lt H. G. McMath (RPCC)

(U) This project has several closely interrelated objectives:

1. To provide an insight into high-temperature and high-pressure reaction kinetics and combustion mechanisms of liquid propellant systems by identification of species generated in a laboratory-scale combustor.

2. To provide an up-to-date thermodynamic equilibrium performance program and thermo-library for theoretical prediction of propellant performance.

3. To determine thermochemical data on advanced propellants and their exhaust species.

(U) Laboratory effort in support of these objectives involves rather sophisticated experimental techniques. A continuous sample of propellants fired in a small, liquid-liquid combustor is taken, line-of-sight, from the combustion chamber, through a differentially pumped sampling system, and analyzed in a time-of-flight mass spectrometer. When possible, an exhaust sample is taken with an evacuated bottle and analyzed by a Beckman GC2A gas chromatograph. Normal test-stand parameters are recorded so that a comparison can be made of mixture ratio and performance to chamber species (or exhaust species). Propellants studied during the past 6 months include the bipropellant combination of hydrazine and chlorine pentafluoride (CPF). The latter study indicated that:

1. No deviation from equilibrium prediction occurs at the stoichiometric mixture ratio (O/F = 2.7).

2. More ammonia is formed in fuel-rich mixtures than is predicted from thermodynamic equilibrium.

3. At very fuel-rich mixtures, the excess hydrazine decomposes to ammonia, nitrogen, and hydrogen in mole ratios of 2:1:1.

4. The amount of ammonia formed in fuel-rich mixtures approaches equilibrium values as the stoichiometric mixture ratio is approached.

5. A deposit, identified as primarily hydrazine dihydrofluoride, is likely to form on any cold surfaces ($100^{\circ}F$ or less) during the reaction of hydrazine and chlorine pentafluoride.

6. The optimized mixture ratio for the hydrazine/CPF injector was very close to the value calculated by the method of Elverum and Morey.

(U) The first phase of a study to compare ammonia production in the catalyzed and uncatalyzed decomposition of hydrazine has been completed. In this first phase, hydrazine decomposition was initiated by a chlorine pentafluoride slug start. Results of seven runs showed that an average of 44% of the total products was ammonia. At this concentration a 10% increase (over equilibrium values) in C* performance was realized. Measured performance was not good due to the fact that a bipropellant injector was used. The same white residue mentioned previously was observed on the walls of the combustor. The low melting point of this solid indicates that the hydrazine decomposition was gas phase.

(U) Certain difficulties have been experienced in the checkout and calibration of the time-of-flight mass spectrometer/shock tube systems. However, they now appear to have been resolved and testing will begin early in January 1968 to assess the system's value for studying the recombination of active species. The test program for this evaluation will use dissociated chlorine, fluorine, hydrazine, and chlorine trifluoride in the temperature range of 1200 to $3000^{\circ}K$. The shock tube will be used to generate known ratios of atoms to molecules. Analyzing these known amounts through the sampling system will provide the means to determine the system's capability for handling labile species.

(U) Other current and planned activities include heat-capacity and volume calibrations on a calorimeter which will be used to measure the heat of formation of xenon hexafluoride; updating of the AFRPL propellant performance computer program to provide information on propellant and propellant combinations of interest to air-augmentation concepts; and the development of performance curves for the CPIA Solid Propellant Performance Handbook.

PUBLICATIONS:

The investigation of hydrazine and chlorine pentafluoride combustion and Phase 1 of the monopropellant hydrazine study have been documented and will appear as an AFRPL Technical Report. A paper based on the hydrazine/chlorine pentafluoride reaction will be presented at the AIAA 6th Aerospace Science Meeting, January 1968.

(U) Altitude Ignition Studies/Project 314803DCN/J. E. Hewes (RPCE)

(U) Space-ambient conditions may cause unstable combustion and ignition spike effects in attitude-control engines. Such effects have been experienced in static testing and mission activities with N_2O_4/N_2H_4 type propellants — and have been counteracted with mechanical fixes accompanied by undesirable weight penalties. The same effects can probably be inhibited or prevented by basic design approaches if sufficient knowledge can be acquired of propellant reactions in engine firings under a space environment.

(U) An AFRPL facility is being developed for the study of combustion initiation and shutdown processes as well as the effects of chemical reaction residues on engine restarts. The facility will be capable of simulating altitudes up to 300,000 feet in a chamber of 160 cubic feet water volume. High-resolution instrumentation will monitor the temperature and pressure transients, during start and shutdown, in the engine and propellant feed system. The effects on the chemical reaction, of flow rate, nozzle area, L*, contraction ratio, flow control, injector design, and chamber material will be studied. A 50-lb-thrust engine will be used in these studies.

(U) After establishing baseline data with state-of-the-art propellants and engine hardware of known performance, new liquid propellant combinations will be evaluated for their comparative performance characteristics.

IN-HOUSE LABORATORY PROGRAM

(U) Solid Propellant Exploratory Evaluation and Development/ Project 314804ACJ/C.G. Bacon (RPCE)

(U) Propellants for future weapon and space systems will need to incorporate advanced fuels, oxidizers, binders, plasticizers and special-purpose additives if they are to meet performance requirements. Special facilities and techniques are needed to safely process and test such materials in the quantities required to characterize them, determine their applicability to system requirements and reveal problem areas. This project provides and utilizes the necessary facilities in support of such objectives.

(U) Early AFRPL in-house work on solid propellants was done in a semiremote facility since it involved only low-viscosity and relatively insensitive double-base propellants using conventional oxidizers and metal hydrides. However, to safely process highly sensitive propellants containing such energetic ingredients as HAP, HP-2, and NF binders required a completely remote facility as well as barricaded remote handling capabilities for processing, transporting and firing grains. The facility is in the buildup phase and when completed will consist of four remote mixing cells, with capacity ranging from a few grams to 30 pounds and including one cell with controlled humidity (~10ppm H_2O); an oxidizer preparation cell; a fuel preparation cell; a motor lining cell; a mandrel insertion and extraction cell; a curing cell; a motor assembly cell and a physical properties cell.

(U) Work under this project over the past 6 months has involved propellant formulation, processing and testing activities in support of various in-house and contractual programs relating to air augmentation, evaluation of PBEP and Telagen, burn-rate modification and gas generator grains for postboost-control-system (PBCS) concepts.

(C) The air-augmentation effort concentrated on high-boron-loaded propellants; the boron content started at the 40% level and was gradually increased to 60%. These high-solid loadings were facilitated by an

AFRPL-developed process for prewetting the boron. Two binders were used, Telagen and PBAN. Additional processing studies are planned which will evaluate other binders and the feasibility of special techniques to increase total solids, and reduce propellant viscosity. A small air-test facility will also be fabricated and selected propellants evaluated for after-burning and residue.

(C) The PBEP studies have involved small laboratory tests to determine the best ratio of polymer to cure agent and preliminary cure studies with hexamethylene diisocyanate (HDI). Mixer breakdown problems were encountered when attempting to process gumstocks. Upon return of the repaired mixer from the manufacturer, gumstocks will be prepared for mechanical property testing and formulation of propellants with hydroxyl-ammonium perchlorate (HAP), hydrazine diperchlorate (HP-2), and aluminum hydride (LMH-1).

(U) Four Telagen polymers (carboxyl-terminated saturated and unsaturated, and hydroxyl-terminated saturated and unsaturated polybutadienes) were obtained from the General Tire and Rubber Company and analyzed. They will be cured with various curing agents, and cross-linkers and physical property measurements will be made using Saylak cylindrical samples. The data will be statistically treated to compare and contrast curing agents, curing sites and polymer microstructure.

(C) Six batches of double-base propellant were prepared and 24 motors tested in support of Project FAST (Foamed Aluminum Solid Testing). A three-fold increase in burn rate was demonstrated without the addition of any burn-rate catalyst. Additional motors will be made using a composite propellant to determine burn-rate enhancement in that type of propellant. Burn-rate catalysts (such as HYCAT, amyl ferrocene, etc.) will also be added to determine any interactions and the maximum burn rate attainable with this concept.

(U) Work on gas-generator grains has been extended to propellant formulation and test motor firings. Data has not yet been reduced.

(U) A program has also been initiated to improve facilities for processing solid propellants on a pilot-plant scale. The improved facility will allow remote processing of Class 7 propellants and enable the handling of new materials from small-scale motors to 10-pound tests in a completely remote manner regardless of sensitivity, toxicity or hygroscopicity of the materials.

IN-HOUSE LABORATORY PROGRAM

(U) Ultra Energy Concepts/Project 314806ACK/Lt H. G. McMath (RPCCR)

(C) Past AFRPL in-house and contractual efforts have been concerned with the treatment of hydrocarbons in a helium-hydrocarbon plasma discharge, thereby obtaining small quantities of solid product having a heat of combustion higher than that of the starting material. In some cases, samples have been produced and reported as having heats of combustion as high as three times that of the starting material. The production of such high-energy material has been quite nonreproducible, largely due to lack of control over the operating parameters (such as electrical configuration, discharge current and frequency, pressure, and ions present in the discharge). In recent months, special effort has been directed toward the quantitative characterization of each parameter by constructing and operating a reactor in which these parameters are closely measured and controlled. Contractual effort to this end has indicated a correlation between the heat of combustion of the treated product and the total discharge current.

(C) The current objective of this project is to study and attempt to verify this observation, also to obtain further reproducibility in the treatment of hydrocarbons in the glow-discharge process with emphasis on correlation of the process parameters with the degree of energy enhancement of the products. The first phase of research toward this objective has recently been completed with approximately 50 samples being produced. Although some increase in the heat of combustion with current was observed, the data exhibit considerable scatter, and the reported correlation was found to be only partially reproducible. No samples were produced with heats of combustion markedly higher than the heat of combustion of the starting material. The second phase of this effort is now in progress. It utilizes a slightly different electrode configuration and the experiments are designed so as to characterize the effect of time (or a reactor conditioning effect between successive

data runs) as well as discharge current on the heat of combustion. A quadrupole mass spectrometer has also been connected to the reactor. This instrument may be used for direct sampling of molecular species during an experimental run or for testing of the reactor for traces of impurities. In order to obtain a maximum amount of information from calorimeter data, a detailed statistical standardization procedure was accomplished. A statistically significant number of samples of the starting hydrocarbon material were then analyzed at random over a time period of 3 months and standard deviations established for the calorimetric procedure.

(C) Beginning with the second phase of the heat of combustion versus curren correlation, elemental analyses are being determined on all produced samples. For this purpose, a Perkin-Elmer Elemental Analyzer is being used; samples are analyzed for percentage of H, C, and N.

(U) PUBLICATION:

The reactor, associated equipment, and experimental operating details will be described in an AFRPL report scheduled for publication in March 1968.

IN-HOUSE LABORATORY PROGRAM

(U) Transtage Catalyst Evaluation/Project 624A00DCM/Lt L. P. Barclay (RPCE)

(U) Current catalytic-type gas generators and thrustors for hydrazine decomposition use Shell 405 catalyst. Relatively little is known about the performance of this catalyst when contaminated. It is known, however, that Shell 405 and several second-generation hydrazine catalysts are on a structurally weak substrate and therefore are susceptible to mechanical damage in most applications.

(U) The second-generation catalysts are more economical than Shell 405 in initial cost but their cold-start capability is low. Proposed thermal catalyst systems require constant hydrazine pulsing to maintain minimum temperature levels. Such systems waste fuel and generate undesirable thrust components. An economical, small, isotopic heat source has recently become available from industry; the use of such a heat source would allow the catalyst to be kept thermally active without pulsing and also would make it possible to use stronger substrate materials then those presently employed. Furthermore, since fairly high temperatures may be obtained with a relatively low-power heat source, an isotopic heater should also be of interest in evaluating the potential of materials, notably molybdenum and certain of its compounds, which demonstrate a limited catalytic activity at ambient temperatures.

(U) This project will study the effects of various contaminants on Shell 405 catalyst. It will also investigate the feasibility of using low-activity materials at relatively high temperatures in a hydrazine catalyst system. The Shell 405 study will include firings in a 5-lb. thrustor after each exposure of the catalyst to a contaminating environment, as well as the determination of engineering property data in accordance with requirements of the Titan III transtage development program.

LIQUID ROCKET SYSTEM TECHNOLOGY

LIST OF ACTIVE CONTRACT PROJECTS AND IN-HOUSE LABORATORY PROGRAMS

LIQUID ROCKET DIVISION (RPR)

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IN-HOUSE LABORATORY PROGRAMS

(This page is Unclassified)

(U) Environmental Research Satellite Propulsion Component Flight Testing/AF 04(611)-10747/TRW Systems - Friction Experiment/ R. L. Hammel, TRW/J. H. Smith (RPRPP)/Heat Transfer Experiment/J. M. Robinson, TRW/D. T. Clift (RPRPP)

(U) The purpose of this program is to conduct a friction experiment and a zero-gravity heat-transfer experiment in an orbital flight test. The objective of the friction experiment is the acquisition of information concerning the surface friction of materials in the space environment. In addition, the experiment is designed for the purpose of calibrating laboratory vacuum chambers against in-space conditions such that more meaningful data can be obtained from future laboratory tests. The objective of the heat transfer experiment is to determine the influence of reduced gravitational acceleration on: (1) the magnitude of heat-transfer coefficients in the natural convection, nucleate boiling, and film boiling regimes; and (2) the heating rates at which transition between these regimes occurs. These data will be compared with ground-test data and analytical predictions, with the aim of establishing relationships describing gravity effects.

(U) On 28 April 67, ERS-20 "Orbital Space Vacuum Friction Experiment" was launched from Eastern Test Range. An elliptical orbit of 50,000 nautical miles (n.m.) apogee and 4000 n.m. perigee was provided by Titan IIIc-Vehicle 10. Launch and tracking were exactly as planned. Spacecraft operations have been flawless.

(C) Extensive flight results on 16 material combinations over an 8-month period indicate a significant difference between actual and simulated space environment for most metallic combinations. Interim flight results cover a range of 0 to 500% friction increase between ground test and flight test. Six of 16 material combinations did not increase in space while several others exhibited a 300 to 500% increase. Four groups of sliding contacts are being evaluated: elemental metals, engineering alloys, self-lubricating solids and thin/solid film coatings. Natural

molybdenum disulphide, of the lubricated systems category, gave the lowest overall coefficient of friction. Of the alloys, stainless on stainless gave the highest frictional values. Tungsten carbide on gold film has been noted to exhibit the same coefficient of friction in air, laboratory vacuum and in space, thereby providing an excellent control and reference. Table I gives a comparison of flight test versus ground tests in an oil-diffusion pumped vacuum chamber at 10^{-8} torr. Data included herein is preliminary. A final report on ERS-20 will be distributed in the summer of 1968.

(C) TABLE I

PRELIMINARY RESULTS - ERS-20 FRICTION EXPERIMENT

(Excerpt from data reported in "Chemical Propulsion Newsletter," Jan 68, Vol 4 - Nr. 1, published by Chemical Propulsion Information Agency, C/o Johns Hopkins University)

TYPICAL MATERIAL COMBINATIONS		AVERAGE COEFFICIENTS OF DYNAMIC FRICTION	
Oscillating Rider	Fixed Specimen	Ground Vacuum (Oil Diffusion) Pumped 10^{-8} torr	Space, 4000K 60,000-mile orbit
440C	X Natural Molybdenum Disulphide	.04	.04
440C SS	X Synthetic Molybdenum Disulphide	.05 - .13	.15 - .6
440C SS	X Teflon (15% glass filled)	.05	.24 (temp dep.)
Aluminum	X Beryllium	.15	.45
440C SS	X Vespel (SP-21)	.13	.28
440C SS	X 17-4PH Stainless Steel	.95	Shear pin release 2.0

(U) The heat-transfer experiment provides for applying incremental heating rates to Freon 114 while monitoring heater temperature, bulk temperature, and system pressure. The duration of each test and the power level will be chosen via command link at the discretion of the experimenter. The system will operate at the spacecraft equilibrium temperature except for a small (less than $5^{\circ}F$) temperature rise during heater operation. Between experiments the temperature of the test liquid will return to vehicle equilibrium temperature, and the battery will be recharged. An acceleration level of the order of 10^{-4}g can be obtained by the ERS spacecraft. The g level will be determined from the spacecraft spin rate as measured by a solar aspect indicator.

(U) The zero-gravity heat-transfer experiment spacecraft has been assembled. Flight qualification testing will begin shortly. The first heat-transfer experiment is scheduled for launch aboard the Titan IIIC-Vehicle 5 in August 1968.

REFERENCE

"Environmental Research Satellites for Space Propulsion Systems Experiments" AFRPL-TR-66-290, AD 801699.

(U) Liquid Rocket System Conjugate Structure and Tankage Program, Part II/North American Rockwell, Inc. - Los Angeles Division/ C.E. Conn/AF 04(611)-10752/C.H. Richard (RPRPT)

(U) This program is the second part of the Conjugate Structure and Tankage Program initiated by the AFRPL which is aimed at the attainment of the features offered by solid-state joining technology for improving mass fraction and liquid rocket tankage structure. The objective of this part was to provide a tankage and structure assembly suitably designed for use as Stage II of the Titan III vehicle. It was fabricated from a standardized geometry of Roll Diffusion Bonded Titanium Truss Core Sandwich structure for use in future planned tests and evaluations.

(U) Essentially, this part of the program consisted of two phases of effort. The first included a study made of the applicability of Roll Diffusion Bonded Titanium Truss Core Sandwich structure to the Titan II Second Stage Vehicle. As a result, the benefits exhibited included weight reductions, increased stiffness, a decrease in length and an integration of the propellant delivery conduits and manifolds with the structure in a unique and multipurpose manner. The completion of the second phase of the program resulted in the following: (1) The development of one type of Roll Diffusion Bonded Titanium Truss Core Sandwich structure of exceptional quality and strength properties at a cost of less than $100 per pound. This cost was achieved by the production of only six developmental packs and includes the normally higher costs associated with prototype development; (2) The design, analyses and successful construction of a full-size 10-ft-diameter tank structure which is suitable for use under the same conditions of loading and flight operating conditions as the current Stage II of the Titan III vehicle and which weighs approximately 50% less; (3) The compilation of a Structural and Functional Testing Plan for use in the scheduled structural verification testing program. (The tank structure will be tested in an FY-68 program.)

(U) The program was completed during September 1967 and the results have been reported in the following reports:

REFERENCES

1. "Liquid Rocket System Conjugate Structure and Tankage", Part I, "Functional Integration and Design Study", AFRPL-TR-65-21, June 1965, AD numbers: Vol 1-465205, Vol 2-465206, Vol 3-465207, Vol 4-465208, Vol 5-465209, Vol 6-465210, Vol 7-465211.

2. "Liquid Rocket System Conjugate Structure and Tankage Program, Part II, Phase I Technical Report, AFRPL-TR-66-142, June 1966, AD 485079.

(U) Free-Standing Pyrolytic Graphite Thrust Chambers for Space Operation and Attitude Control/The Marquardt Corp/J. Campbell/ AF 04(611)-10790/M.F. Powell (RPRRE)

(U) The objective of this program is to determine the feasibility and practicality of using free-standing pyrolytic graphite (PG) thrust chambers for space propulsion systems. The program involves investigation of the material capabilities in various radiation-cooled design configurations and an extensive analytical and testing program with N_2O_4/50% N_2H_4-50% UDMH, LF_2/H_2, and LF_2/hydrazine type propellants.

(U) The high-temperature operating capabilities of pyrolytic graphite coupled with high strength-to-weight ratio, resistance to chemical erosion, and excellent thermal shock properties, offer the potential of operating lightweight thrust chambers at the high combustion temperatures and heat fluxes associated with high-energy propellants. As a result of the highly anisotropic nature of PG, the thermal stresses in a free-standing PG chamber are much more complex than those encountered with more conventional materials and require careful design and manufacturing approaches to insure a structurally sound component.

(U) Phase I, Analysis and Preliminary design, and Phase II, Small Scale Testing, have been completed and reported on in previous contract reports. A problem of high residual stresses, which are formed during the fabrication process, was encountered during Phase II. These stresses caused failure of the altitude thrust chambers. The Phase III effort, Materials and Thrust Chamber Evaluation, is 95% complete. The objectives of Phase III were to obtain additional material properties required to solve the structural problem encountered during Phase II and then to design, fabricate and evaluate thrust chamber assemblies at thrust levels up to 1000 lb. Both continuously nucleated and boron-alloyed PG showed residual stress values significantly less than the conventional substrate nucleated PG. During Phase III one 100-lb-thrust altitude thrust chamber

was successfully fired with N_2O_4/50-50 at 100-psi chamber pressure for 30 sec, indicating that the earlier problems with residual stress had been overcome. Four sea-level TCA were tested with LF_2/MMH at 100-psi chamber pressure and 1000-lb thrust. These chambers were fired for 360, 360, 1000 and 300, respectively. The 300-sec test consisted of 30 (10-sec) pulses. One of the 360-sec tests was with a boron-alloyed PG chamber. The remaining chambers were all continuously nucleated PG. All the chambers were in excellent condition following the tests.

(U) The remaining work consists of testing one chamber at 300-psi chamber pressure with CTF/MMH to investigate the higher pressure capability of free-standing PG.

(U) The following reports have been published under this program AFRPL-TR-66-95, "Free Standing Pyrolytic Graphite Thrust Chambers for Space Operation and Attitude Control, Phase I: Analysis and Preliminary Design", J.G. Campbell et al, June 1966, AD 487431.

AFRPL-TR-67-98. "Free Standing Pyrolytic Graphite Thrust Chambers for Space Operation and Attitude Control, Phase II: Small Scale Testing", J.G. Campbell et al, May 1967, AD 382057.

(U) Maneuvering Satellite Wide-Range Flow Control/TRW Systems/ F. Merritt/AF 04(611)-10819/J.R. Lawrence (RPRPD)

(U) The objective of this program was to provide technology necessary for accurate propellant flow control for a 50:1 throttling ratio, liquid fluorine/liquid hydrogen propulsion system.

(U) The program consisted of three phases as follows:

A. Phase I consisted of a detailed study of parameters that influence throttling and included the evolution of design concept for:

1. Wide-range flow control of cryogenic liquids (LF_2/LH_2) in variable-area cavitating venturis.

2. A control system for maintaining mixture ratio within 1% for the variable-area cavitating venturis.

3. Flow control of cryogenic liquids (LF_2/LH_2) over a 200:1 range in a noncavitating valve. The 200:1 flow-control range is required for controlling propellants to the 50:1 dual orifice engine injector developed on Contracts AF 04(611)-9575 and AF 04(611)-9965.

B. Phase II was based upon the concepts resulting from Phase I and consisted of design and fabrication of the following:

1. Two bipropellant (i.e., dual propellant flow passages) throttling valves for LF_2/LH_2 flow control in a cavitating mode over a 50:1 range.

2. A valve-positioning and propellant mixture-ratio-control system for the above valves.

3. Two single-flow passage test models for experimental investigation of noncavitating flow control of cryogenic fluids over a 200 to 1 flow range. In addition, design changes and modifications were accomplished on the valves developed under Contract AF 04(611)-9100 (reported in Reference 1) to permit flow testing with LF_2.

C. Phase III consisted of performance evaluation of the hardware fabricated in Phase II.

(U) The Phase I study has been completed and the basic design criteria and concepts for the bipropellant (LF_2/LH_2) and noncavitating valves established. Additional data were compiled on the mixture-ratio-control design requirements and the thermodynamic characteristics of supercritical hydrogen as related to throttling processes.

(U) Liquid fluorine flow testing was conducted with the valve developed under Contract AF 04(611)-9100. These tests have demonstrated the feasibility of using a variable-area cavitating venturi to throttle LF_2.

(U) Phase II and III work is completed on design, fabrication, and testing of the bipropellant valve and controller and the 200:1 throttling range noncavitating valve.

REFERENCES

1. AFRPL Quarterly Project Progress Report for October, November, December 1964.

2. AFRPL-TR-68-32, Final Report, "Maneuvering Satellite Wide-Range Flow Control" will be published in April 1968 by TRW, Inc.

(U) Advanced Storable Rocket Technology/Advanced Rocket Engine - Storable (ARES) (Project 682A)/Aerojet-General Corporation/ Rudi Beichel/AF 04(611)-10830/C. D. Penn (RPRA)

(U) ARES (Advanced Rocket Engine - Storable) is a high-pressure, staged-combustion rocket engine which operates with the storable propellant combination N_2O_4/50% N_2H_4-50% UDMH. High performance, light weight and simplicity are emphasized in the design of this 100,000-lb-thrust engine. The objectives of this Advanced Development Program are to demonstrate the critical component technology required for this engine. The areas of effort include the primary and secondary combustors, turbopump housing, pump wear rings, and propellant lubricated bearings.

(C) These tasks have all been successfully completed except for the secondary combustor. The basic problem has been cooling the thrust chamber while still obtaining high performance at the 2800-psia design pressure. The performance goal is 90% of theoretical Isp (280 seconds at sea level); and in order to demonstrate durability, three tests of 20 seconds duration must be made at this performance level. A large part of the difficulty in achieving this goal has been due to incompatibility of the injector with the transpiration-cooled thrust chamber, meaning that nonuniform propellant injection produces fuel-rich streaks which react with the oxidizer coolant. The resulting hot spots increase the coolant requirements and have resulted in chamber damage.

(U) Significant progress has been made in the last 6 months toward attaining the required thrust chamber durability and high performance. A new injector concept has evolved after evaluating several patterns for applicability to the transpiration-cooled thrust chamber. This injector is called the "platelet" injector and consists of a number of vanes fabricated from thin steel plate. The fuel is injected from small orifices at the tips of the vanes while the oxidizer-rich gases from the primary

combustor flow between the vanes. This injector has demonstrated high performance, exceptional durability, and acceptable compatibility.

(U) Forty thrust-chamber tests have been conducted with injectors of this type. Five of these tests were of 20 seconds duration and the others were of approximately 3 seconds duration. The initial tests were made at very high coolant flow rates and then the transpiration coolant was reduced so as to increase the delivered Isp.

(C) The maximum performance with the first thrust chamber tested was 88.5% Isp. Slight chamber erosion occurred when the coolant was reduced beyond this point. A higher performing injector was used with a new chamber and the 90% Isp goal was achieved on one 20-second test. This injector was damaged on a subsequent test when a propellant leak after test shutdown resulted in detonations within the injector. A similar injector was also damaged because of a recurrence of this leak.

(C) The only injector then available for test was the one which delivered lower performance. With this injector, a durability demonstration was accomplished at a performance of 89% Isp. The test hardware was in very good condition after these three 20-second tests. Further coolant reductions were made and the 90% Isp goal was exceeded and verified on three short-duration tests. The actual performance was 90.3% or 281 seconds Isp (sea level). However, when the first of three planned 20-second tests was attempted, a chamber burnout occurred after 7 seconds. This was apparently due to a decrease in coolant flow at this point since thermal steady-state had been established on the successful shorter tests.

(C) One of the higher performing injectors is being repaired and will be available for testing by mid-January, 1968. With this injector, it is expected that the 90% Isp can be achieved at a higher coolant flow. Thus, it is likely that the durability and performance goals will be achieved.

(U) This work will be completed by the end of January 1968. Application studies will then be conducted by the AFRPL to determine the attractiveness of a storable space engine based on the technology generated by this program. Such an engine will probably have a thrust of approximately 50,000 lbs and operate at a lower chamber pressure. It will also be capable of throttling, unlimited restart, and long-term standby in space. A throttling and scaling study of the ARES engine has already been completed. This work was performed on a separate exploratory development contract, F04611-68-C-0008, and is discussed elsewhere in this volume.

REFERENCE

AFRPL-TR-67-75, "Advanced Rocket Engine - Storable", Phase I Interim Final Report, August 1967. AD numbers: Phase 1, Pt 1-383737; Pt 2-383738; Pt 3-383747.

(U) Study and Demonstrate of an Advanced Thrust Chamber Cooling Concept (Project TRANSPIRE)/Aerojet-General Corp/Dr. A. Blubaugh/AF 04(611)-10922/L. E. Tepe (RPRRE)

(U) The transpiration cooling of a porous-wall thrust chamber was investigated on this program. Rocket engine thrust chambers were constructed of stacks of very thin metal platelets or washers containing a series of photoetched passages which allowed a fluid to be bled through the chamber wall to the interior. The overall objective of the program was to investigate this technique of chamber construction in conjunction with using the oxidizer as the coolant fluid.

(U) Two oxidizer propellants, N_2O_4 and ClF_3, were investigated at both 100 psia, 100-lb thrust and 1000 psia, 1000-lb thrust with the propellant combinations of N_2O_4/50% N_2O_4-50% UDMH and ClF_3/MHF-3. The oxidizers were used as the coolants since neither oxidizer exhibits the thermal stability problem associated with hydrazine-type fuels.

(C) A total cumulative firing time of 3070 seconds in 121 tests was achieved on one N_2O_4-cooled, steel-platelet chamber which included 2510 seconds at 100-lb thrust and 560 seconds at 1000-lb thrust without requiring significant repair. In order to reduce coolant flow to that which could be acceptable for an actual application it was found that the oxidizer transpiration cooling concept is very sensitive to chamber surface roughness and injector-chamber compatibility. It was also demonstrated that plugging of the porous wall is not a problem with proper platelet design.

(C) Thirteen tests were conducted with ClF_3-cooled nickel-plated chambers at 100-lb thrust; 23 tests were conducted at 1000-lb thrust. Various problems were encountered. An undetected water leak into the chamber through a failed seal weld in a water-cooled injector attachment flange produced $NiF_2 4(H_2O)$ salts which plugged the chamber wall interior

portion and caused severe erosion on a subsequent test. Another chamber malfunction occurred when the critical coolant lead time on start was not sufficiently increased as coolant flow rate was progressively decreased. Also, exhaust plume attachment at the nozzle exit induced heat input into the platelet assembly in a nonradial direction. This heat input was above the estimated design limit and resulted in erosion of the expansion nozzle and throat station. These problems have been solved through component redesign and by increasing coolant lead time. Additional effort by Aerojet has identified the problem of two-phase flow of the coolant taking place prior to chamber ignition, which in turn causes a liquid coolant lag during the start transient. Proposed solutions to this last problem have yet to be demonstrated.

(U) The test evaluation has verified the steady-state oxidizer transpiration-cooling concept; however, the coolant flow rates as yet have been higher than optimum.

(U) Two reports have been published which describe the program accomplishments. The first report covering Phase I work, AFRPL-TR-66-295, was published in March 1967, AD 380029. The final report, AFRPL-TR-67-198 was published in October 1967, AD 385085.

(U) Fabrication, Test, and Delivery of a Transport/Handling System for Large Solid Rocket Motors/Clark Equipment Company/W. Norlander/ AF 04(611)-11211/L.B. Thompson (RPRPT)

(U) This program began in January 1966. It provides design, fabrication, delivery and test of a vehicle system capable of performing local transport and handling functions required for 120- and 156-inch-diameter solid rocket segments and monolithic motors within a launch facility.

(U) The system was delivered to the AFRPL facility during the latter part of December. It will be assembled and functionally tested during the period of 3 January through 31 March 1968. The system will then undergo an accelerated service test at the AFRPL. This is currently scheduled to be completed by 31 October 1968. The accelerated service test is designed to determine and verify the design efficiency of the system and to establish logistic requirements such as manpower, maintenance, operating costs and general utilization potentials for large overland transport vehicles.

(U) Acoustic Liners/Pratt and Whitney Aircraft/G. Garrison/ AF 04(611)-11387/Capt J. F. Ensminger (RPRRC)

(U) The objectives of this exploratory development program are to: (1) provide a computerized resonant acoustic liner design technique for the engine design engineer; and (2) develop analytical methods and acquire supporting experimental data for the design of effective nonresonant liners.

(U) The program is divided into two phases. Phase I covers the area of resonant acoustic liners and was predicated on the assumption that basic resonant liner feasibility has already been adequately demonstrated. As a result of this phase a report was published containing information on the design of resonant acoustic liners. Since this design technique utilizes a computer program, all necessary data concerning the program will be included in the report (listing input and output formats, flow chart, etc.). A limited amount of cold-flow testing will be done to investigate the acoustic effects of various hole shapes on the absorption coefficient and frequency response of a liner. A hot-firing test program will be conducted to determine the required liner length, best location and absorption coefficient necessary for the effective suppression of combustion instability. All hot firings conducted in this program utilize N_2O_4/Aerozine-50 at chamber pressures of 100 and 1000 psia. Phase II will cover the development of analytical methods for the design of nonresonant liners. Cold-flow experiments using Rigimesh and copper-wafer transpiration-cooled liners are to be conducted in support of the analytical effort. The influence of film cooling as well as out-gassing of ablative resins is to be experimentally determined. Using the derived analytical procedures, nonresonant acoustic liners will be designed and hot-fired to evaluate their effectiveness.

(U) Phase I has been completed; this includes the cold-flow testing of various orifice shapes, the publication of the special report and the completion of the hot firings. The experimental data obtained from cold-

flow tests of elliptical, rectangular and cruciform orifice shapes indicate that present theoretical predictions need to be revised. The special report, "Absorbing Liners for Rocket Combustion Chambers-Theory and Design Techniques" (AFRPL-TR-66-234), has been published and is available from DDC (AD 378329). The Phase I Final Report, "Acoustic Liners for Storable Propellant Rocket Chambers (AFRPL-TR-67-205) is also available from DDC (AD 384580). The Phase I general results established that successful liners must be at least one-fourth of the chamber length, positioned next to the injector face and have at least 23% acoustic absorption.

(C) The film-cooled-liner tests have been completed. The assembly was stable to all pulse guns up to 50 grains in size for fuel coolant flow rates of 0.0, 1.5, 2.0, and 2.5 lb/sec. Pressure traces indicated increased instability as the film-cooling flow rate was increased but in no tests did the pressure oscillation exceed ±5% of chamber pressure (this somewhat arbitrary value is generally used as the limit for stable combustion).

(U) The design of the Rigimesh type acoustic liner has been somewhat unsuccessful. Cold-flow tests have shown the absorption of the proposed liner to be very marginal over the range of frequencies in which this injector has exhibited instabilities.

(U) Some trouble has been experienced in the design of a successful ablative liner. All hot-firing tests to date have been unstable. The latest exploratory tests indicate that out-gassing of the constituents of the impregnating resins have changed the liner design values, thus resulting in low liner absorption characteristics (i.e., unstable operation). Further work is planned to resolve this ablative liner design problem.

(U) Advanced Cryogenic Rocket Engine Program - Aerospike Nozzle Concept/Rocketdyne, Division of North American Rockwell Corporation/R. J. Fontaine/AF 04(611)-11399/Capt V. L. Mahugh (RPREB)

(U) This contract was the Rocketdyne part of the first phase of a two-phase Advanced Development Program to demonstrate a high-performance, throttlable, reusable LO_2/LH_2 rocket engine concept. The purpose of this effort was to evaluate critical technology associated with the annular chamber-aerospike nozzle engine concept. This effort, completed on 31 October 1967, consisted of the following subtasks: Module Design; Applications Study; Injector Performance Evaluation; Thrust Chamber Cooling Investigation; Thrust Chamber-Nozzle Demonstration; and Segment Structural Evaluation. The complete program is reported in AFRPL-TR-67-280.

A. (U) Module Design - The module design subtask provided preliminary designs for the 250,000-lb-thrust engine.

B. (U) Applications Study - The applications study effort provided vehicle performance data for six representative vehicles using the aerospike engine concept. A detailed discussion of this effort is presented in AFRPL-TR-67-279.

C. (U) Injector Performance (2, 500 lb) - Several tests were conducted in support of the 250K task to evaluate the effect of the injector modifications to eliminate thrust-chamber-injector end heating. Performance calculations indicated a significant reduction in combustion efficiency, therefore, the 250K injector pattern was not modified. Steps to eliminate the heated zones in the 250K hardware are presented below. Injector performance data from this subtask are shown in Figure 1.

D. (C) Thrust Chamber Cooling Investigation (2, 500 lb) - The test data analysis of the 314 cyclic tests with a nickel tube wall segment supported the previously observed performance trends of the triplet injector

pattern (97 to 100% C*). The predicted thermal fatigue life was in good agreement with the experimental results. It was concluded that the 300-thermal-cycle life requirement can be achieved with Nickel 200 tubes in the selected chamber configuration.

E. (C) Thrust Chamber-Nozzle Demonstration (250,000 lb) - On 2 July 1967 a major injector failure terminated the third tube-wall chamber test. The test conditions achieved were: 630 psia chamber pressure, M.R. 6:1, and 1.5 seconds duration. It was concluded that the injector failure resulted from propellant leakage at the injector strip end braze joint caused by overheating of the injector strip ends by oxidizer-rich hot-gas flow in the gap between the injector strip ends and the thrust chamber body.

(C) The second tube-wall chamber assembly was modified to provide protection from the oxidizer-rich recirculation gas near the injector face. The coolant tubes were coated with a 0.008- to 0.010-inch zirconia coating for a distance of 1.5 inches immediately downstream of the injector face. A metallic lip seal was installed on the chamber to prevent hot-gas circulation between the injector body and chamber. A sealer (RTV) was added to the inner body behind the baffle to reduce intercompartmental gas flow. Three tests were conducted with the second tube-wall chamber. Hardware inspection after the last test showed the injector face to be in excellent condition, however, erosion had occurred on the sides and trailing edges of the baffles. It is believed that the baffle erosion caused by hot-gas flow was associated with the 1800-Hz rotating combustion wave observed in the tube-wall chamber test films. The erosion damage terminated full-scale testing.

F. (C) Segment Structural Evaluation (20,000 lb) - Testing with the 20K segment hardware showed combustion efficiency varied from 95% at 625 psia chamber pressure to near 100% at the higher chamber pressures. Measured dimensional throat gap during the test series indicated

that no plastic deformation of the structure had occurred. The bulk heat transfer compared favorably with the 2.5K nickel tube-wall segment data. After the final test, the tube bundle was found to have essentially no bond to the epoxy adhesive allowing the tube bundle to bulge in several places because of pressure from tube leaks. The lack of bonding apparently resulted from insufficient bonding pressure during the cure period. Additional segment tests were conducted under a company-funded effort. This test series included a single test for 47 seconds at 1125 psia and a M.R. of 6.23.

(U) This report is the last submission for this contract.

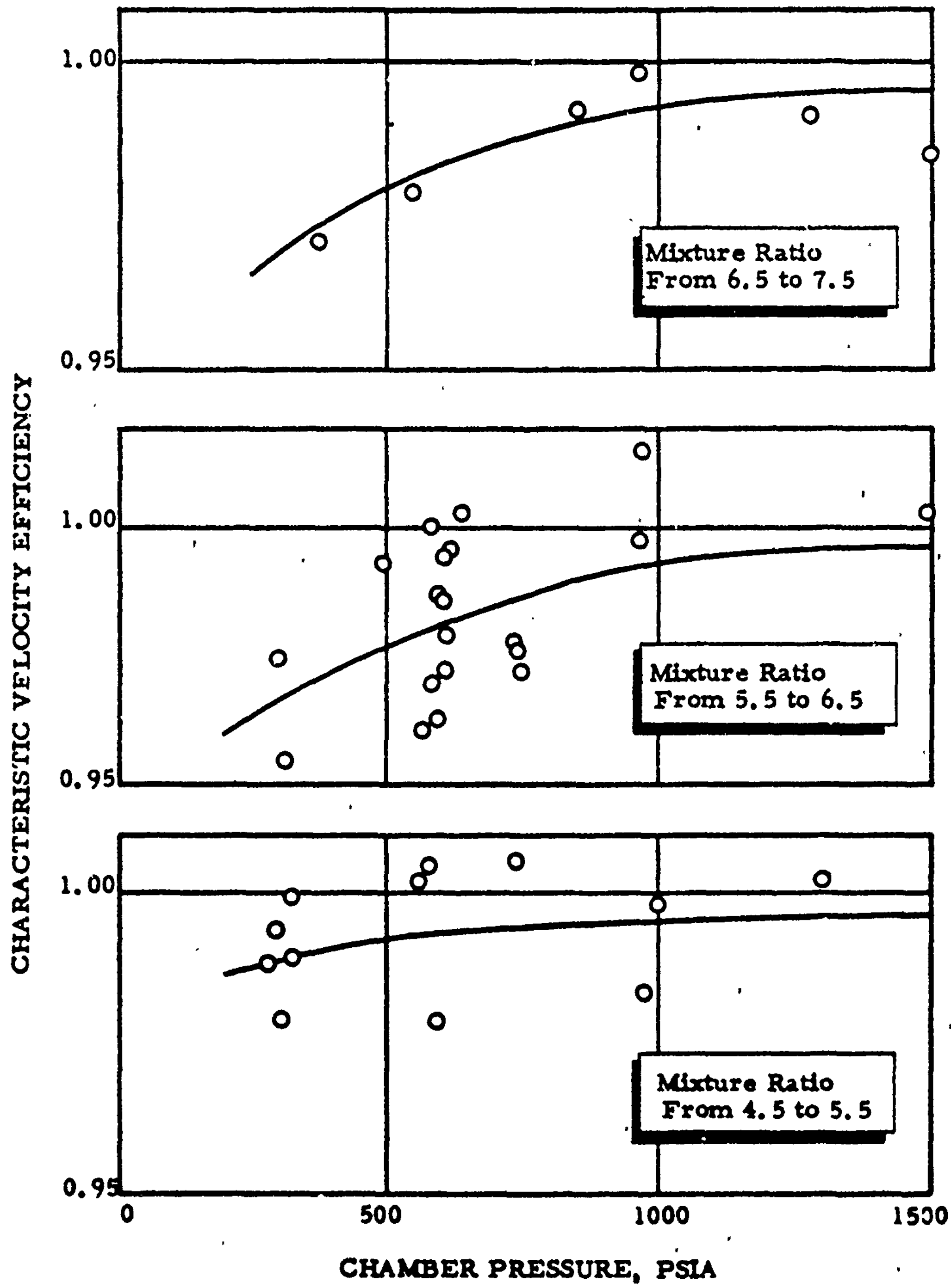


Figure 1. Triplet Injector Performance in the 2.5K Segment Thrust Chamber

(U) Advanced Cryogenic Rocket Engine Program - Staged Combustion Concept/Pratt and Whitney Aircraft/R. R. Atherton/AF 04(611)-11401/ Capt R. E. Probst (RPREB)

(U) This contract was the Pratt and Whitney part of the first phase of a two-phase Advanced Development Program to demonstrate a high-performance, throttlable, reusable LO_2/LH_2 rocket engine concept. The purpose of this effort was to evaluate critical technology associated with the staged-combustion/bell-nozzle engine concept. This effort, completed on 30 September 1967, consisted of the following subtasks: Module Design; Applications Study; Cooling Investigation; Turbopump Components; Module Control System; and Preburner Demonstration. In addition, the contractor furnished main chamber hardware for use in staged-combustor testing with the preburner. The complete program is reported in AFRPL-TR-67-298, AD 385910.

A. (C) Module Design - A revised engine cycle balance was conducted with pump efficiencies reduced from 78% for both turbopumps to 64% for the fuel pump and 68% for the oxidizer pump. In order to achieve constant full thrust (250,000 lb) over the mixture ratio range from 5:1 to 7:1, main burner chamber pressure was reduced from 3000 psia to 2740 psia.

B. (U) Applications Study - The applications study effort provided vehicle performance data for six representative vehicles using the staged combustion engine concept. A detailed discussion of this effort is presented in AFRPL-TR-67-270, AD 385426.

C. (U) Cooling Investigation (50,000 lb) - The cooling investigation with 50K hardware provided data for the design of the 250K transpiration-cooled chamber. Predicted coolant flow rates and performance were verified during 250K staged-combustor testing.

D. (U) Turbopump Components - The bearing configuration chosen for endurance testing used AISI 440C rollers and races and an outer race piloted Armalon cage. A radial interference fit was used to provide roller preload.

(C) The first endurance test was terminated after 15 hours at 48,000 rpm because of roller skewing in the reaction bearing (1485-lb load). Analysis indicated the roller skewing was caused by unloading of the rollers on the side opposite the applied load. The next three endurance tests were terminated, because of roller skewing, at 7.5, 1.25, and 3.75 hours. The reaction bearing used in the final three tests accumulated 12.5 hours of operation at 48,000 rpm and 1485 lb radial load. This completed testing on this subtask although the goal of 10 hours life with 1700 lb radial load at 48,000 rpm was not obtained.

E. (C) Module Control Systems - A total of 41,000 actuation cycles was completed on the preburner oxidizer flow divider valve. Inspection showed excellent wear characteristics of the beryllium copper piston ring on the chrome-coated housing with no pressure differential and increasing deposition of the Be-Cu on the housing as the piston ring pressure differential was increased to 1000 psi. The flow divider valve was used during preburner and staged-combustor testing and the correlation of valve effective area in LO_2 showed close agreement with the water calibration data.

(C) A total of 34,000 actuation cycles was completed on the mixture ratio valve at internal pressures to 4200 psi. Static seal leakage problems were encountered at internal pressures above 3500 psi but disk and shaft seal performance was satisfactory. The mixture ratio valve was also used during staged-combustor testing.

F. (C) Preburner Demonstration (250,000 lb) - The preburner injector was modified to reduce the peak to average temperature profile. Further development is required to reduce the temperature profile to 150°R which is required for the demonstrator engine. Two pulse tests were conducted with hydrogen temperatures near 100°R to demonstrate combustion stability. The chamber pressure disturbances, produced by pulse charges, were damped within 30 ms. Preburner chamber pressure was limited to 3600 psia (72% of the required 5000 psia) because of an inadequate dome flange seal design.

G. (C) Staged-Combustor Demonstration (250,000 lb) - The preburner was combined with full-scale main-burner hardware to demonstrate staged-combustor impulse performance and dynamic combustion stability. A minimum transpiration coolant of 1.0% of total flow was demonstrated at full thrust. Specific impulse efficiencies at the 100% and 20% thrust levels are shown in Figure 1. Dynamic combustion stability was demonstrated in tests conducted at 100% and 20% thrust with charges of 40 and 80 grains fired during each test. In each test, chamber pressure oscillations were damped in 30 ms or less.

(U) This report is the last submission for this contract. The initial effort on the Phase II program is reported under Contract F04611-68-C-0002.

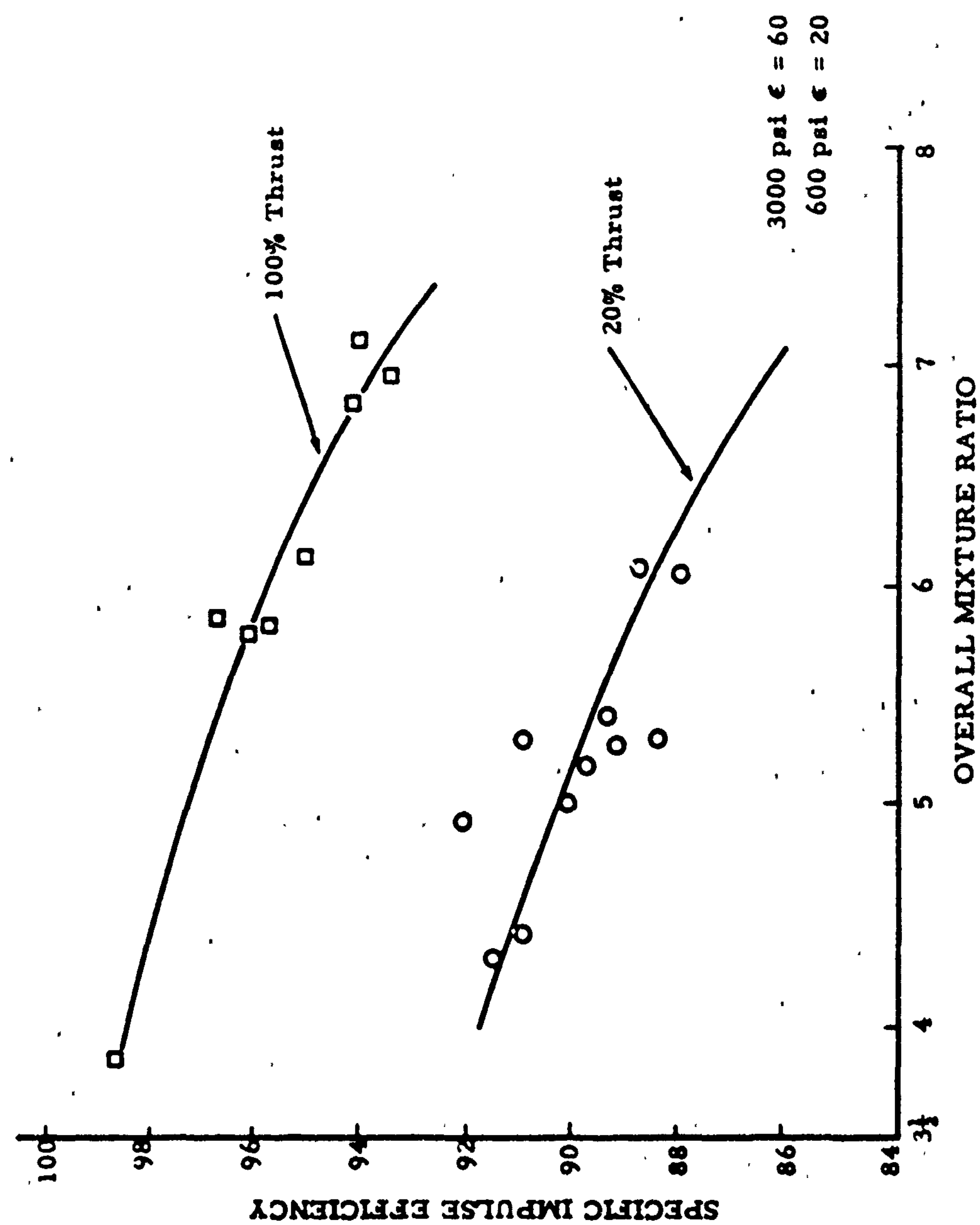


Figure 1. 250K Staged-Combustor Performance

(U) In-Space Propellant Orientation and Venting Experiment/Lockheed Missiles and Space Company/R. Parmley/AF 04(611)-11403/ Lt R. Mears (RPRPT)

(U) The objective of this program is to design, fabricate, and perform qualification testing of a surface-tension propellant orientation and ullage venting experiment for in-space testing.

(U) The data from this experiment will determine the feasibility of utilizing the surface-tension property of liquid propellants in completely passive devices designed to maintain propellant position control in space vehicles. The ability to predict accurately the shape and location of liquid propellants under low-gravity conditions will permit the use of lightweight, highly reliable devices to provide vapor-free propellant for engine operation and to permit the venting of liquid-free vapor, thus avoiding the loss of propellant and vehicle performance. This experiment culminates a program of analytical and experimental research into the behavior of liquid propellants under low-gravity conditions and methods of controlling their behavior. The experimental research, conducted by governmental agencies and industry, consisted of normal-gravity, as well as drop-tower and zero-gravity aircraft testing.

(U) The experiment design is such that the limits of propellant-vapor interface stability can be demonstrated by subjecting the test tank to varying acceleration levels in varying directions. An electric motor drive is used to vary the acceleration vector relative to the test tank. Acceleration magnitude is varied by control of the spin rate of the spacecraft in which the experiment is installed. Data will be primarily acquired in the form of television or photographic recording of the fluid behavior. A multiple-mirror installation will permit viewing all points of interest (in the test tank and connecting fluid lines) from a single camera. An accumulator tank is included to permit multiple fluid expulsion from the test tank. This feature will permit repeating tests to increase confidence in the

results and performing additional tests as deemed desirable, based on test results.

(U). The fabrication of the surface-tension experiment has been completed. The qualification testing of the prototype unit and the flight unit was completed successfully. After completion of the qualification tests "Lock-Tite" lubricant was put on the bolts holding the "Lexan" domes to the center plate assembly. Stress corrosion occurred at the bolt holes and was proven to have been caused by the "Lock-Tite". New domes are being fabricated and will be installed in February 1968. The experiment will be delivered to the AFRPL upon completion and installation of the new domes.

(U) The experiment was assigned a Category I priority "Program Objective Essential" by the Space Experiment Support Program, but to date it has not been assigned to a flight.

REFERENCES

"Phase I Final Report, In-Space Propellant Orientation and Venting Experiments", AFRPL-TR-66-270, 31 October 1966, AD 804224.

(U) Decomposed Ammonia Radioisotope Thruster (DART) Program/ TRW Systems/F.A. Jackson/AF 04(611)-11536/Lt D.A. Shantz (RPREA)

(U) The objective of this contract is to develop the Decomposed Ammonia Radioisotope Thruster (DART). The DART uses energy from the decay of a radioisotope to heat and decompose ammonia propellant prior to expansion through a nozzle. Both the heating and the decomposition increase the specific impulse obtainable with this propellant. The specific objectives of this contract were to identify missions for which DART is superior to other forms of propulsion and then to design and demonstrate a flightweight thruster.

(C) The original contract was completed in March 1967, however, not all the objectives of the program were met. A mission study was conducted and certain missions were identified for which the DART system was either superior or competitive with other low-thrust propulsion systems. Using the results of this study and of a concurrent parametric design analysis, a detailed thruster design was generated.

(C) A demonstration thruster was fabricated and delivered to the Atomic Energy Commission's Mound Laboratory, where a 24-day test was performed with the thruster at operating temperatures for approximately 300 hours. In this test, the heat source and thermal insulation met or exceeded all test objectives, however, leaks developed in the flow tubes, preventing the determination of thrust and specific impulse, and the platinum-10% rhodium flow tubes did not decompose the ammonia.

(U) The demonstration thruster has been placed in a vacuum test chamber where it will be maintained at equilibrium temperature for several months to determine the long-term performance of the heat source and thruster components.

(U) Since the original objectives of the program were not met, TRW Systems resumed work on the contract in November 1967. The additional work includes a brief design effort to improve the DART configuration in addition to braze and flow-tube material tests. A braze material will be found which will not vaporize at the high DART temperatures, and a flow-tube material will be found which will decompose the ammonia. After a new DART thruster is fabricated, it will be tested with an electrical heater prior to delivery to Mound Laboratory. At Mound the radioisotope source will be added and a 3-week test will be performed.

(U) To date, TRW Systems has initiated the thruster redesign, and the braze material and ammonia decomposition tests. The additional work on this contract is scheduled to be completed with the demonstration test of the new thruster on 15 June 1968.

(U) Propellant Feed System Storability Demonstration/General Dynamics-Convair/R. White/AF 04(611)-11545/Major R.B. Tanner (RPRPT)

(U) The objective of this program is to provide subscale prepackaged liquid propulsion subsystem test articles to determine the storability of various tank pressurization systems and components with rocket propellants for periods of up to 5 years. The test articles, when delivered, will be placed in a controlled environment and periodically subjected to simulated operational conditions such as vibration. At selected intervals, test articles will be operated to evaluate their performance after storage.

(U) In Phase I, the contractor will design, fabricate, and assemble 24 propellant tank subsystems, each containing an expulsion device, surface-force orientation (SFO), or rolling diaphragm and other required components. Phase II will provide for design, fabrication and assembly of 24 pressurization systems: solid propellant gas generator, liquid propellant gas generator, and stored gas system. Phase III will involve integration of tankage and pressurization subsystems, loading with ClF_5, N_2O_4, or MHF-5, and delivery of systems to the AFRPL for in-house testing.

(U) The contractor has completed work on this contract. One system loaded with ClF_5 ruptured at the contractor facility. Postrupture examination indicated a leak in the rolling diaphragm and reaction of the ClF_5 with the silicone rubber to evolve gas. A decision was made not to load RD systems with ClF_5, but to use NASA Spec N_2O_4 instead. The remaining 23 systems have been delivered to AFRPL for in-house testing.

(U) Advanced Thrust Chamber for Space Maneuvering Propulsion/ Rocketdyne - H.G. Diem/AF 04(611)-11617/W.W. Wells (RPRES)

(C) The overall objectives of this program were to perform analytical studies and to develop technology applicable to a space maneuvering propulsion system that employs an LF_2/LH_2, toroidal aerospike thrust chamber. The program was divided into three tasks with only analytical mission studies being performed under Task I. Tasks II and III demonstrated the performance, stability, throttlability, cooling and structural integrity of aerospike thrust chamber segments. Task I results have already been summarized in a previous report and will not be discussed here.

(C) During Tasks II and III, over 150 thrust chamber tests were conducted and all program objectives were met. A throttling range of 9:1 was demonstrated, and delivered C* performance exceeded the 97% contract requirement over the whole range. Tapoff gas temperature and flow rate control were also demonstrated. Thrust chamber segments were regeneratively cooled successfully using two-pass coolant (H_2) flow. Thrust chamber structural integrity was demonstrated in a final test series of Task III where throat area changes of less than 5% were obtained over the whole throttle range.

(U) The program was completed as scheduled in June 1967 and was accomplished within the original contract funds. The final reports for Tasks II and III of the program were distributed in July 1967 as AFRPL-TR-67-214, AD 383164 and AFRPL-TR-67-226, AD 383260. The final report for Task I had been distributed in September 1966 as AFRPL-TR-66-301.

(U) This will be the final semiannual summary report written on this program.

(U) Hybrid Propulsion System for an Advanced Rocket-Powered Target Missile/United Technology Center/R.A. Jones/AF 04(611)-11632)/ F.B. Mead (RPRRC)

(U) The objective of this program is to develop and fabricate 15 identical flight-weight hybrid propulsion systems suitable for use in a target missile vehicle. Five of these units were mated with missile airframes procured from Beech Aircraft Corp. under AFATL contract and flight tested to demonstrate flight feasibility. Ten propulsion units were delivered to the AFRPL for flight certification testing under Project 573002CRQ (Hybrid Target Missile).

(U) The program is being conducted in four phases. Phase I consists of hardware and tooling design and fabrication. Interface definition between the Beech airframe and the UTC propulsion system was finalized. During Phase II, heavyweight propulsion systems were cold-flowed and hot-fired to obtain design data for finalization of the flight-weight propulsion system configuration. Flight-weight system testing was then conducted under simulated altitude and environmental conditions to insure that the hybrid propulsion system met the specifications set forth by the Air Force. Phase III included the fabrication, assembly and delivery of propulsion units to the AFRPL and Beech Aircraft. In Phase IV, the contractor will provide technical support to the AFRPL and Eglin AFB during the system certification testing and flight test programs, respectively.

(U) On 12 December 1967, the first hybrid target missile was successfully flown at Eglin AFB, Florida. The missile flew under powered flight for 260 sec at 49,000 ft. Prior to this test all phases of this program had been successfully accomplished including certification at altitude of the propulsion system by the Air Force at the Rocket Propulsion Laboratory.

(U) Serious technical difficulties in the hybrid propulsion system development were not encountered until flight-weight testing was initiated.

During the heavyweight testing of the TCA it was considered adequate to test at the minimum and maximum thrust conditions, thus bracketing all levels of system performance. Such was not the case, as tests with the flight-weight system showed and later computer studies verified. Regression rates did not vary at intermediate thrust levels as predicted from heavyweight tests. Burnthrough of the engine case occurred in several missions. Corrective action included the addition of a silica phenolic insulator sleeve over the fuel grain and an off-loading of 10 lb of oxidizer. Some reshaping of the combustion chamber's head end was also required to enhance ignition and avoid excessive heat soak-through in the area of the injector. It was also determined by test data that the system could not be fired at the maximum required temperature of 165°F. At this temperature and operational chamber pressures, conditions existed that caused the oxidizer to flash to a vapor in the feed system prior to reaching the injector. However, operation of the final configuration was not impeded by this problem since actual launch and storage conditions for this demonstration model were significantly less stringent.

(U) Flight testing is presently continuing at Eglin AFB with flights scheduled to altitudes of 80,000 ft and speeds of Mach 3.0. To date the propulsion system has performed as expected and meets the Air Force requirements for this flight demonstration program.

(U) The following reports have been published under this contract:

1. AFRPL-TR-66-286, "Hybrid Propulsion System for an Advanced Rocket-Powered Target Missile", November 1966, AD 377469.

2. AFRPL-TR-67-54, "Hybrid Propulsion System for an Advanced Rocket-Powered Target Missile", February 1967, AD 379425.

3. AFRPL-TR-67-153, "Hybrid Propulsion System for an Advanced Rocket-Powered Target Missile", April 1967, AD 381591.

(U) Fabrication and Test of Pneumatic Handling Device for Large Solid Rocket Motors/Presray Corporation/B. Watson/AF 04(611)-11695 and F04700-68-C-0208/L.B. Thompson (RPRPT)

(U) This program provides for the design, fabrication, and test of a unique device to provide safe and expeditious handling of large, solid rocket motors. The device will be integrated and tested as a part of a large, solid rocket motor transport and handling system being developed for the AFRPL.

(U) The device, referred to as a "Pneumagrip", consists of a hydraulically operated opening-and-closing cylinder, which is positioned around the various motor segments and latched closed. Pneumatic tires, arranged within the interior of the device are then inflated so as to grip the motor segment and permit lifting in either the vertical or horizontal attitude and during transport.

(U) The handling device has been delivered to the AFRPL and has successfully completed a preliminary design acceptance test. Final testing will be completed during the 1 April - 31 October 1968 accelerated service test of the large rocket transport and handling system at the AFRPL facility.

(U) Development and Demonstration of Ablative Thrust Chamber Assemblies Using LF_2/N_2H_4 Blend Propellants/Aerojet-General Corp. - C. Williams/F04611-67-C-0003/L.E. Tepe (RPRR)

(U) The objective of this program is to demonstrate long-duration capability with restarts of an ablative thrust chamber assembly using fluorinated propellants and to demonstrate high performance.

(U) The specific design parameters were selected to demonstrate the potential upper-stage application of a composite ablative chamber for a pressure-fed propulsion system using a fluorine-based oxidizer. Selected operating conditions and design conditions are:

Propellants	LF_2/N_2H_4 Blend*
Chamber Pressure	100 psia
Thrust, Vacuum	7,000 to 8,000 lbs
Mixture Ratio	1.91
Duration	600 seconds total
Restarts	5
Thrust Chamber Assembly Length	81.6 in. total including valve and nozzle
Max. Nozzle Exit Dia.	47.1 in.

* BA1014, Wt. Percent: 66.7 N_2H_4, 24.0 MMH and 9.3 H_2O

(U) The program is being accomplished in three phases. Phase I, which has been completed, consisted of the design and analysis for the thrust chamber assembly components. Phase II, presently being conducted, includes the fabrication, test, and evaluation of injector patterns, selected ablative chamber materials and designs, and a coated-columbium radiation-cooled nozzle extension. Phase III will include the evaluation

of an acoustically damped chamber and higher performance injector pattern combination.

(U) The Phase I report, AFRPL-TR-67-52, AD 811911, with the same title as the program, was published in March 1967. The report covers the component design and analysis accomplished in that phase.

(U) During the initial injector test evaluation portion of Phase II, combustion instability was encountered. The two injector patterns originally built and test-fired were both unstable in the first tangential mode. The injector patterns consisted mainly of triplet, two fuels on one oxidizer, elements. The first injector, built of aluminum to economically establish fabrication procedures, contained 215 elements. The second injector contained 158 elements and was built of nickel which is more durable with the higher heat flux and higher chemical activity associated with the combustion environment of the selected propellants. The 158-element injector was successively modified to a 68-element configuration which had stable combustion but gave lower performance than the preceding configurations. In simulated altitude tests, this injector was used to establish the 600-second-duration capability of an ablative composite thrust chamber containing a fibrous graphite throat insert. The chamber configuration consisted of a phenolic-impregnated graphite-cloth cylindrical section insulated in turn by phenolic-impregnated carbon cloth and silica cloth. Posttest evaluation of the chamber is in process. After the 600-second duration the total throat area increase, including some gouging resulting from injector streaking, was less than 7%. The other composite chamber configuration which will be evaluated on the program has a full-length fibrous-graphite liner from the injector end to an expansion ratio of 1.65 to 1.

(C) The original Phase III on the program involved altitude-simulation testing of a thrust chamber assembly consisting of a flight-type valve, a more optimum chamber design based on Phase II results, the best

injector and a full-length radiation-cooled nozzle extension. However, the performance attained with the stable injector pattern, which gives about 94% C*, is below the performance goal of 370 seconds specific impulse. Phase III was therefore redirected to the investigation of an acoustically damped chamber designed to use the fibrous-graphite material which has good strength at high temperature (4500°F). An injector pattern which will give better mixing and better compatibility through finer elements more evenly spaced across the injector face will be built. The analysis of the new pattern presently being considered indicates that the 370-second Isp goal will be attained.

(U) Nuclear Weapon Effects on Rocket Propulsion Systems/McDonnell Douglas/J. Watcher/F04611-C-67-0006/J. Branigan (RPRPT)

(U) The objective of this effort is (a) to assess the vulnerability and failure modes of components of selected future rocket propulsion systems as a function of the radiation spectral component and radiation pulse over a broad range of values; (b) to assess the vulnerability of two advanced propulsion systems when used with the appropriate weapon system components to a specific nuclear environment; (c) to suggest approaches to reduce the vulnerability as appropriate, and (d) to identify areas of extreme uncertainty and define additional experimental or theoretical effort required. The program consists of three phases. Phase I is to apply current data and knowledge of nuclear weapons effects to the components, parts, and materials of advanced propulsion systems and arrive at radiation-dose-level thresholds at which these elements of the propulsion system will (1) surely work, and (2) will surely fail. Phase II is to identify the requirements for additional analytical and experimental effort needed to evaluate the vulnerability of future rocket propulsion systems. Phase III is to assess the survivability of two postboost propulsion systems (PBPS) for early weapon system application.

(U) Significant progress has been made in gathering information on the propulsion systems under study and the available data on the response of materials and construction and propellants to nuclear weapons phenomena. Information has been obtained from numerous governmental and industrial sources active in the field of nuclear weapons effects.

(U) The results of this program will be presented in a final report 26 August 1968. The report will include the Nuclear Weapons Effects Data Handbook and the Program Plan for future work required. A verbal report on the Program Plan is planned to the DASA committee for Propulsion Systems in June 1968.

(U) Application of the Sensitive-Time-Lag Theory to Combustion Instability Studies/Aerojet-General Corporation/J. McBride/F04611-67-C-0019/Capt J. F. Ensminger (RPRRC)

(U) The objectives of this program are (1) to compile theoretical and experimental analyses on the sensitive-time-lag theory into a single design document for general understanding and use by the liquid propellant rocket propulsion community; and (2) to extend the existing experimental correlations for use with the sensitive-time-lag computer program. The program consists of four tasks:

Task I - Compilation and extension of correlation between experiment and theory.

Task II - Extensions to the theory, and refinements to the existing computer program solutions. Extensions to the theory include the non-linear effects caused by the dynamics of the combustion process and the effects of higher chamber Mach numbers. All computer programs and subroutines are combined into a consolidated intrinsic-stability program.

Task III - Presentation of a design report on the sensitive-time-lag theory. The report includes such sections as background, theory development, theory extension, computer program, and realistic examples on use and interpretation of the theory.

Task IV - Instruction of the AFRPL engineer on the use of the computer program and the delivery of the computer program to the AFRPL.

(U) The program is nearly completed; Tasks I, II and IV are completely finished and Task III lacks only the review of the report. The correlation technique is not sensitive enough to differentiate between the various types of injector patterns. The analytical extensions to the theory (Task II) extended its useful range up to chamber Mach numbers of .5. These

extensions should make the theory more useful for practical engine design applications. The computer program has been sent to the AFRPL and is presently being checked out at the AFRPL computer center.

(U) Reports published:

AFRPL-TR-67-314, "Application of Sensitive-Time-Lag Theory to Combustion Instability Studies, Final Report", January 1968, Confidential, Aerojet-General Corp., F04611-67-C-0019.

(U) <u>Trimode Rocket Propulsion Feasibility Demonstration/Bell Aerosystems Company - M. Drexhage/F04611-67-C-0020/P</u>. C. Erickson (RPREA)

(U) The Trimode program will demonstrate feasibility and define operating characteristics of a bipropellant engine which uses the decomposition products from two monopropellant reactors as propellants. The engine is designed to operate in the bipropellant mode, however, it can be operated in either monopropellant mode (N_2H_4 or H_2O_2). The engine is thus multiply redundant by design, eliminating the need for redundance in propellant valving.

(U) Phase I of the two-phase program was completed in July 1967. A technical report summarizing this effort has been published and distributed: Report No. AFRPL-TR-67-293, AD 385593.

(U) Planning and negotiations for the expanded Phase I effort were completed in September 1967. Phase IA will concentrate on injector improvements, minimum L* potential and higher Pc (250 psia). The objective is to further refine the overall concept to provide lower thrust chamber heat rejection rates, faster response and improved efficiency. Phase IA will additionally improve the overall technical value of Phase II. All Phase IA test hardware has been designed and manufactured. Testing was initiated in December 1967.

(U) In Phase I, it was suspected that delayed propellant mixing was responsible for the high thrust chamber heat rejection rates. To support the design of the Phase IA hardware, the contractor conducted a series of tests to define the controlling design parameters for improved gaseous mixing in the shortest length. Mixing length as a function of stream impingement angle and velocity ratio is shown in Figure 1. Mixing length is most affected by stream velocity ratio, a fact incorporated into the design of the Phase IA injectors. These tests also demonstrated that the Phase I injectors did not achieve complete propellant mixing within the chamber length available.

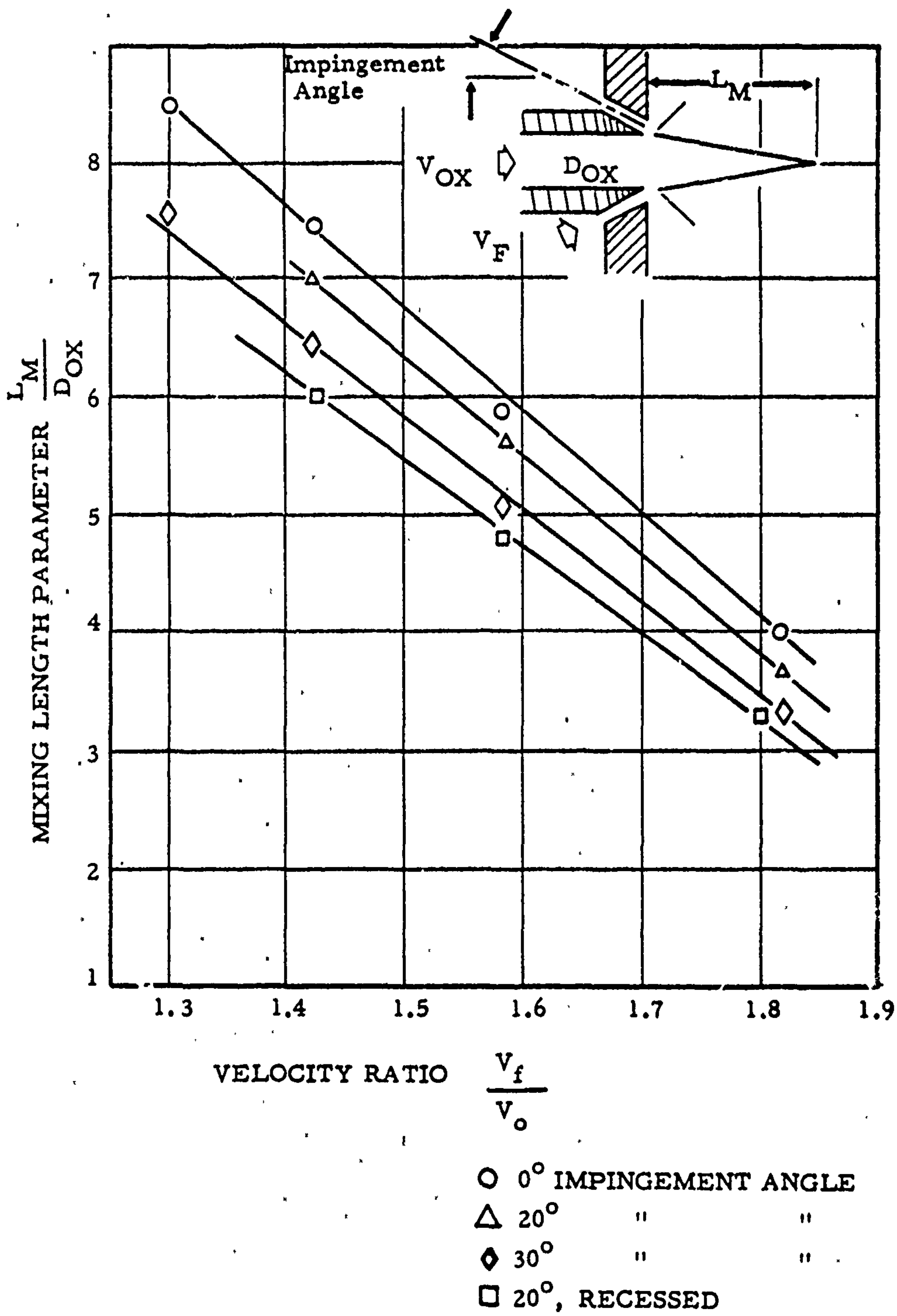


Figure 1. Coaxial Element Mixing Tests

(U) High-Energy Propellant Beryllium Thrust Chamber Technology/ Rocketdyne Division of North American Rockwell/F. Campagna/ F04611-67-C-0024/Capt C.W. McLaughlin (RPRRE)

(U) The objective of this program is to determine the permissible operating regimes of the beryllium thrust chamber concept using propellant combinations of ClF_5/mixed hydrazine fuels, gaseous F_2/gaseous H_2, and LF_2/LH_2 at thrust ranges of 25 to 10,000 lb and chamber pressures of 50 to 1,000 psia. The technical effort of the program, consisting of two phases, was completed on 30 September 1967. Phase I, Preliminary Investigations, included the analysis, design and supporting laboratory testing to permit prediction of the operating limits of the beryllium thrust chamber for steady-state and transient operation. Phase II, Design and Test Evaluation, consisted of the detailed design, fabrication and testing of the beryllium thrust chamber assemblies with ClF_5/MMH to provide empirical verification of the Phase I results. An assessment of operating regimes and recommendations for design points for systems applications were accomplished based on the results of Phase I and Phase II.

(U) During Phase I which was completed in April 1967, data was obtained from tensile, fatigue, strain-rate and thermal-shock tests. In addition, studies were conducted on the effectiveness of various hydrazine blend fuels as boundary-layer coolants and the effectiveness of various materials to protect the beryllium chamber from the severe chemical combustion environment of fluorine-based propellants. It was found that hydrazine hydrate (52% N_2H_4-H_2O, 48% MMH) showed improved cooling performance over MMH and MHF-3. Nickel was found to give excellent protection to beryllium in an HF environment. Finally, predictions of permissable operating regimes of beryllium thrust chambers with ClF_5/MMH, ClF_5/MHF-3, and F_2/H_2 were made in Phase I. A Phase I report, AFRPL-TR-67-150, AD 815012L, was published in May 1967.

(C) During Phase II, three injectors (96 self-impinging doublets with 64 boundary-layer coolant holes), four copper chambers and two beryllium chambers were designed, fabricated and tested with ClF_5/MMH and ClF_3/MMH at 1000 pounds thrust and 300 psia chamber pressure at sea-level conditions. Initial testing with the copper chambers provided detailed performance and heat-transfer data. The majority of tests were conducted with ClF_3/MMH as an economical substitute for ClF_5/MMH. During these tests the boundary-layer coolant flow (BLC) was varied from 10 to 40%. There was approximately a 2% loss in specific impulse performance at 30% BLC. Performance was also found to be relatively insensitive to mixture ratio variation. A $4\frac{1}{2}$-inch chamber length from injector face to the nozzle throat was found to be optimum. Based on these results, two beryllium thrust chambers were designed, fabricated and tested. The first beryllium thrust chamber tested had a 3-inch chamber length and was coated with nickel in the chamber section. Six tests were conducted, with the final test being a duration run at a mixture ratio of 1.34 and 34% BLC. The C* efficie cy was 93% for this test, and the test was terminated after 96 seconds, when the BLC effectiveness dropped off and the nozzle throat temperature began to rise rapidly. Some throat erosion was observed during a posttest inspection, and the nickel coating was found to be in good condition. The second beryllium chamber had a $4\frac{1}{2}$-inch chamber length. Nine tests were conducted with the final duration test lasting only 7.5 seconds. The BLC of 47% could not provide sufficient cooling for any longer duration.

(C) At the conclusion of Phase II, the thermal analysis method was modified and new permissible operating regimes in terms of thrust and chamber pressure were determined. Infinite steady-state operation is predicted for thrusts less than 300 pounds and chamber pressures of 50 psia or less. Run durations are limited for thrusts and chamber pressures greater than these values. The final report, AFRPL-TR-68-1, will be published in January 1968.

(U) System-Coupled Dynamic Instability Amplitude-Limiting Analysis and Evaluation/Martin Marietta Corporation - Denver, Colorado Division/L. E. Fidler/F04611-67-C-0031/C. H. Richard (RPRPT)

(U) The purpose of this program is to provide a more complete definition to the problem of limiting amplitude and the control of longitudinally coupled, dynamic instability in liquid propellant rocket vehicles.

(U) Results from flight-test data have shown that the operation of large liquid rocket vehicles has been significantly hampered by the onset of longitudinal dynamic oscillations and accelerations. Most of the disturbance has occurred in the frequency range of 2 to 30 cycles per second at magnitudes of accelerations greater than $\frac{1}{4}$ units of gravity.

(U) An understanding of the causes and the means for prevention of this type of dynamic instability has been partly achieved. Analytical techniques by which this type of instability can be studied have been surveyed and the development of a digital computer program has been accomplished under Contract AF 04(611)-9956 with General Dynamics/Convair. The computer program is limited to determining the linear stability characteristics using frequency response and root locus techniques for a coupled system comprised of structural, engine, and pneumatic system elements. The feasibility of using small-scale test configurations to define the parameters critically affecting longitudinal stability was developed by Martin Marietta under Contract AF 04(611)-10795. This program has been confined to the development of subscale test methods and configurations as well as an analysis of suction line dynamics, cavitation of turbopumps and the compliance generated by gas pressurization systems. Methods have not yet been fully developed for predicting and controlling the magnitude of the instability oscillation amplitudes and their levels of acceleration once they occur.

(U) This program was performed in two phases. The first required formulation of an analysis to predict: (a) system storability; (b) the amplitude of the uncompensated natural oscillations; and (c) the control of the oscillation amplitude by compensation techniques and devices. The second phase required the analysis to be evaluated by means of laboratory testing using an existing simulator, and then verified by correlation of the test data. The program is 95% complete and has resulted in the publication and distribution of AFRPL-TR-67-231, Phase I report dated August 1967. A final report is expected to be available for publication and distribution sometime during March 1968.

REFERENCES

1. "A Study of System-Coupled Instability Analysis Techniques", Final Report, AFRPL-TR-66-143 (Parts I & II), July 1966, Part I-AD 485312, Part II-AD 485313.

2. "System-Coupled Dynamic Instability Amplitude-Limiting Analysis and Evaluation", Phase I Report, AFRPL-TR-67-231, August 1967, AD 818477.

(U) Combustion Instability Analysis at High Chamber Pressure/ Rocketdyne Div. /Dr. D. Campbell/ F04611-67-C-0036/Lt C. J. Abbe (RPRRC)

(U) A program was initiated 1 December 1966 with the objectives of developing an analytical model of the combustion instability process at high (supercritical) chamber pressures, and verifying the model using available high-pressure experimental instability results.

(U) In meeting the above objectives the contractor is modifying the Priem-Guentert mechanistic analytical model originally formulated at NASA, Lewis Research Center. This model has been utilized by several workers with reasonable success. In the original formulation, droplet temperatures remained at their steady-state values, droplet shattering was not considered, and injection of unburned propellant was unaffected by pressure or time-delay considerations. The modifications being incorporated in the model by the contractor are designed to extend the model to higher (supercritical) combustion pressure by eliminating these restrictions and considering a number of other improvements such as:

1. (U) Droplet Heating - The restriction that droplets remain at steady-state temperatures has been removed. This has introduced new terms into the energy equations to account for the sensible heat of the spray. Likewise, the liquid density can no longer be considered constant, especially near the critical point. Variable droplet temperatures also result in the vapor pressure changing considerably, which may have a significant effect on calculated results.

2. (U) Supercritical Combustion - When liquid propellant droplets now pass through the critical point and gasify, combustion rates will no longer be controlled by vaporization, but rather by an approximate mixing-rate-limited model. This is an important improvement at or above the critical point.

3. (U) Droplet Breakup - Shattering or breakup of propellant spray droplets due to gas velocity waves associated with the instability has been added to the model. A Weber number criterion based on experimental data from the literature is used as a criterion to determine whether or not shattering will occur. Because experimental work shows that the secondary drops produced upon breakup are very small, they are assumed to "burn" instantaneously in this improvement.

4. (U) Concentration of Unburned Propellant Spray - Past versions of the Priem-type model have not adequately considered the major influence of the actual instability pressure waves on subsequent injection of unburned propellants into the sensitive combustion zone. The contractor has formulated an approximation to the phenomenon which considers the delay between injection of propellant into the chamber and its arrival at the combustion zone. This improvement should yield more valid (computer) instability responses to the initial disturbance.

(U) In addition to the above changes, the program is being written to include the effects of both oxidizer and fuel combustion. Past models have always assumed one propellant controlled the overall response.

(U) To support the modifications being made to the instability model the contractor has also gathered from the literature (or estimated) appropriate physical property data for N_2O_4/Aerozine-50 propellants. These data have been gathered in the attempt to improve the accuracy of the data at high pressures. Secondly, during the last 2 months of the contract, several improvements made to the instability model will also be applied to a vaporization-rate-limited steady-state combustion model. Use of this second model is necessary to conduct stability analyses with the instability model. At the completion of the program, the models will be verified using high-pressure storable propellant stability results obtained from in-house project 305804BRI. The contractor has published a Phase I report,AFRPL-TR-67-222, AD 817963, which describes model improvements in more detail.

(U) Study and Evaluation of Segmented-Sphere Pressure Vessel/ ~~LTV Aerospace Corporation/J.W. Farrell/F04611-67-C-0040/~~ C.H. Richard (RPRPT)

(U) The purpose of this program is to determine the structural characteristics and efficiencies of segmented spherical pressure vessels through analysis, fabrication, and test.

(U) High-pressure gaseous and liquid storage containers in the past have been difficult to integrate efficiently into missile and launch vehicles. This has been due primarily to their shape (spherical or cylindrical) and their weight, resulting in the requirement for a large amount of installation space and adequate structure for support. Several small containers manifolded together have been used to alleviate this situation; however, this can result in additional leakage and reliability problems. In an effort to improve this condition, the Air Force Rocket Propulsion Laboratory has initiated a program to investigate segmented spherical containers. They can be fabricated into a variety of shapes which will permit more efficient installation without incurring leakage or a loss of reliability. Preliminary analysis also indicated that weight reductions of as much as 20% over manifolded spheres and 40% over cylindrical tanks can be obtained through the use of this concept. A weight reduction of 40% has also been predicted for the toroidal TVC tanks being used on a large solid motor.

(U) Essentially, the feasibility of joining spherical containers together to form segmented spherical pressure vessels with the equivalent volume capacity at the same design pressure as a conventional pressure vessel has been investigated and the following features have been indicated:

- Minimum weight
- Pure biaxial tension loading in the structural shell materials

- Reduction in material inefficiency inherent with nonuniform strains
- The elimination of internal strain incompatibility
- The opportunity to assemble various spheres with unequal diameters into a random configuration of segmented spheres
- The opportunity to utilize the low-weight high-strength features of filament-wound fibers in pressure vessel designs.

(U) This program is being conducted in three phases of effort. In the first phase analytical and design techniques have been developed to predict the performance and produce three specified types of segmented-sphere pressure vessels. It included the preparation and submittal of a tooling and fabrication manufacturing plan and a test verification and performance evaluation plan. Three pressure vessel designs with sizes between 12 and 36 inches in diameter were selected to permit the use of previously qualified hardware and tooling. The second phase of the program is currently being conducted where the fabrication-manufacturing plan is being implemented to produce one of each of the specified types of segmented-sphere pressure vessels. The result of the progress accomplished to date has been reported in AFRPL-TR-67-261 dated November 1967. In phase III the verification test and performance evaluation plan shall be implemented whereby the adequacy of each of the pressure vessels produced shall be demonstrated and their performance shall be evaluated. The program is approximately 70% complete.

REFERENCE

"Study and Evaluation of Segmented-Sphere Pressure Vessels", Phase I Technical Report, AFRPL-TR-67-261, November 1967, .D 823809.

(U) Vent-Free Fluorine Feed System/Martin Marietta Corporation/ D. Murphy/F04611-67-C-0044/Lt T. J. Kelly (RPRPP)

(U) The objective of this program is to investigate a thermodynamic liquid vapor separator heat exchanger system which will efficiently maintain a vent-free fluorine condition by using the heat-sink capacity of vented hydrogen.

(U) The contractor is conducting a parametric analysis of the heat exchanger methods, fluid inlet conditions, duty cycle and tank pressure level for an F_2/H_2 vehicle. A performance trade off and screening analysis will be conducted culminating with the preliminary design of the most promising system. In addition, the contractor will design and fabricate a test article for use at the AFRPL where testing will be conducted in the Laboratory's 30-foot space-simulation facility. The test article will be used to verify the analysis and determine experimentally the merit of utilizing a thermodynamic separator heat exchanger vent system for application to a fluorine nonvent system.

(U) Results of the parametric analysis, system selection, and preliminary design are reported in Volume I of the program final report.

REFERENCE

(U) "Vent-Free Fluorine Feed Systems", AFRPL-TR-67-323, March 1968

(U) Test and Evaluation of Nozzle Insert Materials Using Fluorinated Oxidizer and Hydrazine Fuel Propellants/Aerojet-General Corporation, Sacramento, Calif/R. Kotfila/F04611-67-C-0053/Lt D. L. Riedl (RPRRE)

(U) The objective of this program is to establish properties of potential insert materials and determine their performance in thrust chambers using high-energy fluorinated oxidizer and hydrazine fuel propellants. The results of this program will be applicable to postboost propulsion systems, upper-stage engines and space engines.

(U) The test conditions of the contract specify 3000-lb thrust and 200 to 300 psia chamber pressure using CTF/N_2H_4 blend and LF_2/N_2H_4 blend propellants. The duty cycles require a 300-sec total duration using CTF oxidizer and a 600-sec total duration using LF_2 oxidizer. Both duty cycles will have multiple restarts. In June 1967 analytical work began on the designs for these conditions. G-90, a bulk graphite and AGC-101, a pyrolyzed and graphitized graphite-cloth laminate were the materials Aerojet selected to evaluate.

(U) The nozzle inserts have been fabricated and are being placed in the insert holders and instrumented. Shipment of the inserts to the AFRPL for testing is scheduled to begin in mid-January 1968. Testing will be contingent upon the planned 1 March 1968 completion of the injector checkout cycle.

(U) No reports have been published on this work.

(U) Test and Evaluation of Nozzle Insert Materials Using Fluorinated Oxidizer and Hydrazine Fuel Propellant/Philco-Ford Corporation, Newport Beach, Calif./R. Hale/F04611-67-C-0060/Lt D. L. Riedl (RPRRE)

(U) The objective of this contract is to establish properties of potential insert materials and determine their performance in thrust chambers using high-energy fluorinated oxidizer and hydrazine fuel propellants. The results of this program will be applicable to postboost propulsion systems, upper-stage engines and space engines.

(U) The test conditions of the contract specify 3000-lb thrust and 200 to 300 psia Pc using CTF/N_2H_4 blend and LF_2/N_2H_4 blend propellants. The duty cycles require a 300-sec total duration using CTF oxidizer and a 600-sec total duration using LF_2 oxidizer. Both duty cycles will have multiple restarts. Analytical work on insert designs to meet these conditions began in June 1967. The materials selected by Philco for evaluation were: (1) Pyrolytic graphite (PG) washers; (2) Super Temp pyrolytic graphite bonded felt and (3) Union Carbide pyrolytic graphite bonded fibers.

(U) The nozzle inserts have been fabricated and the PG washer inserts are at the AFRPL. The rest of the inserts will be shipped in the near future. The beginning of testing is planned for 1 March 1968, but is dependent on the completion of the injector checkout cycle.

(U) No reports have been published on this work.

(U) Fluidic Controls for Advanced Throttling Concept/Bowles Engineering Corp./J. Sims/F04611-67-C-0065/... Mickola (RPRES)

(U) The objective of this program is the development of a pure fluid control system to control injector mixture ratio, momentum ratio and thrust for a 50-to-1 throttling dual orifice injector.

(U) Phase I studies and preliminary design were completed in July 1967. The work is now concentrated on component development through breadboard tests. The development of the control valve amplifier, chamber pressure control and pressure reference circuits has proceeded satisfactorily, however the development of the injector momentum optimizer circuit has experienced difficulties. The circuit is designed for a nominal response of 2 cps and to control injection momentum at engine chamber pressure as low as 6 psia. At the low chamber pressure, signal-to-noise ratio has become critical because of control circuit noise and noise generated by the engine. Efforts to increase the signal-to-noise ratio have shown some improvement, however the circuitry is affected by engine noise having a frequency of 1 to 2 cps. To circumvent a lengthy development period for the optimizer circuit, the contractor has been directed to delete the optimizer circuit. The resulting control system will have the capability of maintaining mixture ratio constant over the entire throttling range, while injection momentum will be preprogrammed as part of control system design.

(U) Development difficulties have caused an estimated delay of 7 months to the program, with technical completion now scheduled for mid-September 1968.

(U) Improvement of Combustion Stability Rating Devices/Rocketdyne/ P. Combs/F04611-67-C-0073/T.J.C. Chew (RPRRC)

(U) The objectives of this program are to improve the reliability and effectiveness of nondirectional bomb and pulse gun as rating devices by eliminating their major design deficiencies, and to define procedures and techniques for effectively applying these rating devices.

(U). Limited analyses of the bomb and pulse gun have been performed to determine the functional characteristics of these rating devices as affected by environmental and operational conditions. Analytical and experimental efforts are being conducted to investigate the effects of bomb case erosion and charge temperature on generated disturbances, the propagation characteristics of the bomb blast wave, and the characteristics and limitations of bombs smaller than 5.5 grains. Similar efforts are being undertaken to determine the effects of pulse gun barrel configuration on the propagation of pulse pressure waves and the influence of burst diaphragm temperature and breech volume on resultant pulse gun disturbances. Reduction of the mechanical complexity, increased repeatability of generated disturbances, and elimination of the burst diaphragm seal leakage problem are also desirable improvements for the pulse gun device. Minimization of the damaging effects of bomb shell fragments is being investigated by considering various candidate bomb shell materials.

(U) In an effort to improve pulse guns, a simplified gun breech and a radially scored burst diaphragm have been designed, fabricated and tested. The new breech functioned adequately and the wave pattern emanating from the pulse gun barrel was approximately spherical for all pulse gun orientations. In an attempt to improve repeatability, pulse guns containing high explosives (PETN) also were designed and tested. The wave shape in the gun barrel for large explosive charges was double peaked similar to the wave generated by the pulse gun using rifle powder. However, the initial shock formed in the combustion chamber by firing the high-explosive

charges was single peaked. In contrast to the rifle powder, the amplitude of the wave generated by the high expl. sive depends very little on the size of the burst diaphragm. Work is continuing with these devices.

(U) Certain nondirectional bomb tests have also been conducted under this program. An analysis of bomb shell erosion and explosive heating was completed to study the factors affecting thermal detonation of bombs. Calculations were made for three bomb-shell materials: teflon, nylon, and reinforced phenolic. It was found that quite-thin bomb shell thickness can provide the necessary thermal protection against thermal explosions. Preliminary shrapnel damage tests were also performed with thin-wall nylon bombs. The apparatus for conducting these tests consists of an 8-inch-diameter cylindrical "cage" made of $\frac{1}{4}$-inch steel rods lined with stainless steel sheet metal. Damage to .012-inch-thick stainless steel was found to be significant for nylon bombs as small as 2 grains.

(U) Finally, an improved bomb has been designed and fabricated for testing. The design seeks to eliminate the structural complexity associated with the use of commercial detonators, either by themselves or with additional explosives, within a protective case. In this manner it is hoped to improve the directional pattern of the disturbance generated by the bomb. Initial results are encouraging; however, testing will continue.

(U) Study of Droplet Effects on Steady-State Combustion/Rocketdyne/ W. Nurick/F04611-67-C-0081/Lt C.J. Abbe (RPRRC)

(U) A 14-month technical program was started 15 March 1967 with the objectives of extending and improving existing correlations between injector-induced spray parameters and combustion performance for a wide range of injector configurations. Specifically, the individual extent of influence of injector mass and mixture ratio distribution and spray drop size on combustion performance is being determined utilizing several combustion chamber lengths.

(U) For any combustion chamber geometry, injector spray drop size, mixture ratio distribution and mass distribution predominately control combustion performance. Thus the approach taken in this contract has been to experimentally measure mass and mixture ratio and drop size distributions using cold-flow propellant simulants, and determine performance by conducting hot-firing tests. Droplet size measurements were made early in the program using an electrostatic probe technique (see AFRPL-TR-66-152, Vol II) but, due to difficulties, are now being made using a frozen wax procedure. This technique makes use of high-temperature "melted" wax which freezes in the air after impinging with either itself (self-impinging elements) or water (unlike-impinging elements) but before contacting the collection trays. Data reduction is conducted by sieving. Drop size results appear to be very satisfactory. Mass and mixture ratio measurements are being made using water/trichloroethylene propellant simulants and an improved version of conventional test-tube-type collection grids. The three important spray parameters (drop size, D_{30}; mixture ratio uniformity, E_m; and mass uniformity, σ) are being measured as a function of element type and design and overall mixture ratio. About 80 hot-firing tests (5000-lb thrust) using N_2O_4/Aerozine-50 propellants are being conducted over the same range of conditions. Table I lists the type of injectors that have been tested and ranges of hot-firing

results. Though cold-flow data are not presented, it is evident that a wide range of element types and spray characteristics are being studied. Fabrication and testing of two additional designs will complete the testing phase of the program.

(U) Experimental data will be correlated in such a manner as to indicate the influence of injector design and operating variables on spray parameters which in turn will be related to combustion performance. As a valuable guide and correlating tool, a vaporization rate-limited steady-state combustion model is being modified to account for nonuniform mass and mixture ratio distributions across the injector. When these modifications are complete, extensive data analysis will commence. Preliminary results confirm trends noted by other workers that larger drop size, poorer mass and mixture ratio uniformity and shorter chambers all tend to reduce combustion performance.

(U) No formal reports have been issued yet by the contractor.

TABLE I

Injector Type	Chamber Length	Mixture Ratio Range	Range of C* (%)
200 element like doublet, zero fan spacing	1 & 6 inches	1.1 to 2.9	92 to 96
200 element like doublet, .35 inch fan spacing	6 inch	2 to 3	89.9 to 90.4
12 element like doublet zero fan spacing	6 to 16.4 in.	.97 to 2.95	66 to 92
12 element like doublet .15 inch fan spacing	6 inches	1 to 2.9	68 to 79
12 element like doublet .35 inch fan spacing	6 inches	1.2 to 2.8	58 to 65
90 element unlike doublet	6 inches	1 to 3.5	92 to 99
39 element unlike doublet	6 inches	1.1 to 3.6	90 to 99
50 element 4 on 1 unlike	1 to 10.4 inches	"	89.7 to 100
10 element 4 on 1 unlike	1 to 16.4 in.	1 to 2.9	74 to 97
single element 4 on 1 unlike	6	1 to 2.5	61 to 83

(U) Cryogenic Propellant Gaging System/General Nucleonic Corporation/ K. Hoalst/F04611-67-C-0091/O. Dyes (RPRPP)

(U) The objective of this program is to design, fabricate, and ground-test a prototype propellant gaging system capable of operating with high-energy, cryogenic, liquid fluorine (LF_2) and liquid hydrogen (LH_2) propulsion systems for future upper-stage and/or space vehicles.

(U) The technique of nucleonic gaging is essentially based on the attenuation and scattering of electromagnetic radiation from a completely safe gamma ray source mounted external to the LH_2 tank and inside the LF_2 tank. Measurement is made by a sodium iodide scintillation detection system mounted external to the propellant tanks. A portion of the gamma rays penetrate the tank walls and supporting structures, and is received by the detector unit. With no propellant in the tank this signal level represents tank-empty conditions and compensates for all mass between the source and detector, except for the propellant. When propellant is added, the signal level received by the detector unit decreases by an amount proportional to the mass of propellant in the tank.

(U) The detector design has been completed as originally scheduled; however, there are problems of instabilities associated with the scintillation detector components (i.e., crystal, photomultiplier tube, high-voltage power supply, preamplifier, and discriminator circuit). For example, the efficiency of the sodium iodide crystal fluctuates with temperature. The output of the photomultiplier fluctuates with both temperature and count rate. Also, the high-voltage supply, preamplifier, and discriminator are subject to fluctuations due to temperature. This problem was alleviated by using the sum and difference technique. The sum and difference technique was a reference source of radioactivity to develop a unique signal which is used as a control reference. When the system is turned on, it is designed in such a manner that it will seek out this reference signal. Once the system has found the reference signal, it operates in a gain stabilization mode.

(U) The detector design is primarily composed of a photomultiplier and a sodium iodide scintillation crystal with an AM241 source imbedded in the crystal. The scintillator-photomultiplier combination converts the gamma from the source into electronic impulses suitable for processing by subsequent electronics into pounds of propellant. It should be noted that pure sodium iodide is being used as the scintillator to take advantage of its high efficiency at cryogenic temperatures. However, a heater blanket and controller are being used to protect the phototube against unknown temperature environments. The temperature is controlled to within $\pm 5^{\circ}K$.

(U) Detector electronics are scheduled to undergo laboratory breadboard testing in January 1968. In addition, temperature tests of the entire detector electronics system and long-term stability tests will be performed. The remaining portion of the breadboard test program, scheduled for completion in February 1968, includes the cryogenic testing of the detector to demonstrate its ability to function as designed in the cryogenic environment. The final prototype is being fabricated for test in May 1968. The final report on this effort is scheduled for distribution in June 1968. No other reports are available.

(U) Compound A/Hydrazine Engine Design Study/Aerojet-General Corporation/W. Luscher/F04611-67-C-0092/E. C. Barth (RPRA)

(U) The primary objective of this effort was to determine the performance, weight and size of a general class of Compound A/Hydrazine engines and to delineate, within the class, the limitation of practical designs in terms of chamber pressure, cooling technique, throttling, etc. Secondary objectives were to identify, from a design standpoint, the critical components and areas of technology which will most seriously affect the capabilities of Compound A/Hydrazine engines and to recommend the most promising or probable cooling technique and method of chamber pressurization (pump versus pressure-fed) to be used for several applications. This study has been completed, and the final report will be distributed by 15 April 1968.

(U) The following range of engine design variables was considered in the study:

Thrust	10,000 to 70,000 lb
Chamber Pressure	100 to 1500 psia
Throttling capability	1:1 to 10:1
Number of restarts	0 to 30
Chamber pressurization	Pump fed - Pressure fed
Fuel	Hydrazine; MMH; MHF-5; N_2H_4-NH_3 blend 80-20%

(U) Eight basic engine configurations were selected within this range and a specific point design studied for each engine. The characteristics of these engines and an estimate of their delivered specific impulse are shown in Table I. Based on these configurations, parametric design data were developed over the range of thrusts and chamber pressures which were applicable for each type of engine. These data include engine performance, weight and envelope.

(U) The problem of selecting the best cooling technique and chamber pressure for a given application received major emphasis in the study. The cooling techniques which were considered included regenerative, transpiration, film, ablative, radiation, and combinations of these. Operating maps were produced which allow selection of the cooling approach for a particular thrust size and chamber pressure. In general, this portion of the study showed that regenerative cooling is limited to the intermediate chamber pressures. At the higher pressures, above 700 psia, transpiration cooling will be required, and at low pressures the passive cooling techniques are more attractive.

(U) The study also identified areas where experimental investigations are required to verify the study assumptions and to provide technology advances which could improve engine performance. These include the effects of chamber/injector geometry on performance, use of high-temperature materials for cooled chamber construction, and improvements in throttling control devices.

TABLE I

COMPOUND A/HYDRAZINE ENGINE DESIGNS

Point Design	Thrust lbs	P_c psia	Feed System	Cycle	Cooling	Throttling	Thrust Chamber Isp sec (ϵ = 150)	% Theo. Isp (TC)	Engine Isp sec
1	10,000	100	Pressure	-	Radiation	Throttlable	330	89.0	330
2	10,000	100	Pressure	-	Ablative	Fixed	325	88.7	325
3	30,000	600	Pump	Gas Generator	Radiation	Fixed	340	92.4	339
4	30,000	600	Pump	Gas Generator	Ablative	Throttlable	338	92.0	337
5	25,000	500	Pump	Gas Generator	Regenerative (liq. fuel)	Fixed	346	92.5	345
6	40,000	1500	Pump	Staged Combustion	Transpiration (liq. oxid.)	Throttlable	347	92.1	347
7	40,000	1500	Pump	Staged Combustion	Transpiration (gas. fuel)	Throttlable	358	96.1	358
8	70,000	1500	Pump	Gas Generator	Transpiration (liq. oxid.)	Fixed	347	92.5	344

(U) Demonstration of a High-Chamber-Pressure Regeneratively Cooled Thrust Chamber Concept/Rocketdyne Division of North American Rockwell Corp/D. Goalwin/F04611-67-C-0093/R.A. Silver (RPRRE)

(U) This contract is the United States share of a cooperative program with the Federal Republic of Germany conducted under Annex No. AF-67-G-7408 to the Mutual Weapons Development Master Data Exchange Agreement.

(U) The objective of this joint program is to demonstrate the technology and capability of milled-copper thrust chambers to operate fully regeneratively cooled at high chamber pressures.

(U) Under this Annex agreement, Boelkow GmbH, under contract to the German Ministry of Defense, will design and fabricate three injectors, two heat-sink thrust chambers and six regeneratively cooled thrust chambers. This hardware will be designed for operation at 30,000 pounds thrust, a mixture ratio of six and a chamber pressure of 3000 psi using liquid hydrogen and liquid oxygen as propellants. This hardware will be delivered to Rocketdyne for testing.

(C) The work to be performed by Rocketdyne on this contract includes providing technical assistance to Boelkow in the areas of injector design, injector fabrication, and thermal instrumentation; performing heat-transfer and stress analyses on the Boelkow designs; testing the hardware; testing the cooled and uncooled hardware; providing the data analysis; performing a limits analysis for the milled-copper-chamber concept, and coordinating a combined US/FRG final report. To date, the technical assistance to Boelkow has been completed, as have the heat-transfer and stress analyses of the Boelkow designs. The uncooled chambers, first two injectors and first two cooled chambers have been received from Germany. The uncooled testing to characterize the two injectors has just been completed, but final reduced data is not yet available. Preliminary

results show the uncorrected C* efficiencies to be over 95% of theoretical with no injector streaking.

(U) This program will be completed during the next reporting period. No reports have been generated to date under this work.

(U) Small Droplet Measuring Technique/TRW Systems/B. Matthews/ F04611-67-C-0105/Lt C.J. Abbe (RPRRC)

(U) A 12-month feasibility demonstration program was initiated in May 1967 to find the best way to detect and analyze liquid rocket engine injector sprays. The objectives of the program are:

(a) to establish the most applicable techniques for detecting and recording sprays down to small sizes;

(b) to demonstrate the feasibility of the most appropriate experimental technique for conducting rocket engine spray studies;

(c) to improve the methods of data reduction.

(U) The program is being conducted in two phases. The Phase I effort, which has been completed, has served to identify a laser holographic technique coupled with a fiber optic data reduction device as most applicable to the unique problems associated with measuring dense high-speed sprays accurate to small (hopefully 10-micron) sizes. During the Phase I effort, seven techniques were investigated (largely through the literature) a potentially applicable to the measuring problem at hand. They are discussed below:

1. Electrical/Electrostatic: These techniques make use of the fact that electrically charged sprays can be electronically counted, and that the electrical signals noted by appropriate sensing equipment are a function of drop size. Rapidity of measurement and ease of data reduction are advantages, while inapplicability to the hot-firing situation and poor resolution are disadvantages.

2. Deposition and Collection Methods: Actual collection and study of "frozen" drops has been used to measure sprays. If appropriate fluids

(such as waxes) are chosen, freezing can occur in ambient conditions prior to the spray contacting any collection vessel. Data reduction can be done by sieving or manual counting. These techniques are not applicable to the hot-firing situation, and it is difficult to find appropriate propellant simulants which will freeze and also have the same physical properties as actual propellants.

3. Light-Scattering Techniques: Light-scattering techniques can be used to measure Sauter mean-diameter drop-size averages directly under appropriate conditions. Several problems, including inapplicability to the hot-firing situation make it unattractive for this program.

4. Fluorescent Photography: By exciting properly dyed sprays with appropriate radiation (as from a Q-switched laser), droplets can be made to radiate themselves, thus acting as their own light source. This is an advantage in terms of improving resolution, but inapplicable to the hot-firing engine. In addition, excitation alignment problems can be significant.

5. Streak Photography: Streak photographs of spray droplets can be obtained by moving film at right angles to a slit, thus recording both size and velocity. Though the system is applicable to the hot-firing situation, resolution is very poor and data reduction is difficult.

6. Spark Shadowgraphs: Conventional spark shadowgraphs, and/or laser backlighted photographic techniques have been used to conduct high-resolution studies of sprays so long as spray fluxes and flame light are not too high. Use of a laser can improve the results because of its short exposure time and high intensity. Data reduction of the resultant photographs is difficult.

7. <u>Laser Holography</u>: This technique is being pursued in Phase II as the most applicable technique. Use of the laser provides for a high-intensity short-duration light source, which makes the technique potentially applicable to a hot-firing environment. Use of holography eliminates the depth-of-field problem associated with conventional photography.

(U) Preliminary tests using the laser holographic technique for observing single-element cold-flow sprays have been highly successful. Resolution is currently about 25 microns diameter. For the remainder of the program, the apparatus will be improved and tested under more severe cold-flow conditions, in an attempt to define its characteristic capabilities and limitations.

(U) An associated effort is also being conducted in Phase II to assemble and demonstrate the feasibility of reducing droplet size information from photographs using a fiber optic scanning device. This apparatus measures light-intensity gradients across the photograph and converts these signals to droplet diameter dimensions utilizing a computer program. Development will continue for the remainder of the program.

(U) An Interim Technical Report is being issued entitled, "Small Droplet Measuring Technique", AFRPL-TR-67-295.

(U) Demonstration of Bipropellant Gas Generator Technology for Air Augmentation Applications/The Marquardt Corp/D. Phillips/ F04611-67-C-0110/Lt W.E. Spangler (RPRRC)

(U) The objective of this exploratory development program is to demonstrate the feasibility of fuel-rich liquid bipropellant gas generators, using interhalogen oxidizers and a boron-loaded fuel, for application to air-augmented rocket propulsion systems. Boilerplate tests, over a range of chamber pressures and mixture ratios, will be made using MARNAF-731 (73% B + 27% Trimethylhexane) and chlorine trifluoride to evaluate performance of the gas generator. These performance tests will be followed by hot-air (direct-connect) tests to evaluate secondary air-gas generator exhaust combustion efficiency.

(C) Three boilerplate gas generators have been designed and fabricated. Preliminary checkout tests have provided data over a range of mixture ratios (0.039 to 0.54) and chamber pressures (72 to 700 psia) with durations up to 14 seconds. Extensive measurements of the exhaust were made to provide a preliminary estimate of the feasibility of secondary combustion of the exhaust products with air. These measurements included gas and particulate exhaust product composition and exhaust particle size and distribution. Residue deposition (B_4C) did occur in some of the tests at higher O/F and P_c operating conditions. Based upon these results a configuration has been chosen for future performance characterization and durability testing (150 seconds duration).

(U) Theoretical fuel pyrolysis calculations are being made on the IBM 7040 computer at the RPL, utilizing the Marquardt finite-kinetics computer program. The 1027 possible pyrolysis reactions have been examined and screened down to 89 basic reactions. Thus, the composition of the gas generator effluent vapors is being determined as a function of time, temperature, and pressure. These results will be used to guide the direction and the interpretation of the experimental effort.

(U) The ignition and combustion characteristics of the gas generator exhaust stream, when mixed with air, will be determined in the direct-connect tests. These tests will be made using an afterburner ducted-rocket configuration, and operating conditions that are similar to those used in other Air Force-sponsored programs. Thus, a direct comparison can be made between the performance of this bipropellant system and the performance of ducted rockets using solid propellant and hybrid gas generators.

(U) No reports have been published to date under this program.

(U) Demonstration of Hybrid Gas Generators for Air-Augmented Rocket Applications/Lockheed Propulsion Company/R. Scobee/F04611-67-C-0111/Lt. W.E. Spangler (RPRRC)

(U) The objective of this exploratory development program is to determine the capability and the applicability of a hybrid rocket as the primary gas generator in an air-augmented propulsion system. A highly boron-loaded solid fuel, obtained from a fuel formulation and characterization investigation, will be used with chlorine trifluoride (ClF_3) and bromine pentafluoride (BrF_5). The experimental gas generator evaluation will determine regression characteristics of the fuel, oxidizer/fuel ratio response, low oxidizer mass flux operation characteristics, hardware durability, fuel utilization, and scaling characteristics. These gas generator tests will be followed by hot-air direct-connect tests to evaluate secondary air-gas generator exhaust combustion efficiency.

(C) Theoretical thermochemical performance calculations have been made to evaluate hybrid solid fuel candidates. Specific impulse performance for ClF_3 and BrF_5 was essentially equivalent, although the higher density of the BrF_5 is favorable from a packaging consideration. Thermochemical calculations to evaluate afterburning potential have indicated that afterburner conditions, primarily temperatures, will be favorable for efficient combustion. Processing techniques involving the boron, the fuel binder, and several additives have been investigated to produce candidate formulations which allow economical processing of grains. The maximum attainable boron content, due to processability constraints, was 79.5 percent. This level is further reduced by the additive requirements in practical fuels.

(U) Special consideration has been given to the surface reactions that could lead to grain sintering and adverse regression behavior. This problem was studied theoretically by imposing conditions of pressure and temperature, assuming thermochemical equilibrium, and calculating

the composition of products emanating from the fuel grain surface. Thus, the relative quantity and composition of gas-phase products was determined and used to estimate drag/weight ratios available for ejecting boron particles away from the fuel surface and into the free stream. The surface reaction problem was investigated experimentally in laboratory fuel slab burner tests and in arc furnace tests. Color motion photographs of the fuel surface were made and used to study this effect. The problem of binder and additive selection to promote acceptable regression rate and efficient combustion was also investigated both analytically and with laboratory slab burner and arc furnace tests. However, the bulk of the combustion screening experiments were motor firings in 2.5-inch-diameter (15-inch length) hardware.

(C) Several gasifying ingredients were incorporated into the solid fuel to investigate their ability to promote the efficient transport of boron particles from the fuel surface to the exhaust stream. Ammonium perchlorate (AP) provided the most efficient boron expulsion.

(U) The solid fuel selected for further subscale testing contains 68%B/14%AP/18% Carboxyl Terminated Polybutadiene (CTPB). The regression rate provided by this propellant is consistent with the magnitude required for a single circular port grain configuration in the full-scale (150 seconds duration) motor design. Theoretical performance calculations with this selected formulation, and with both ClF_3 and BrF_5, were made to estimate specific impulse values for a range of operating conditions and air/propellant ratios. Equilibrium and T-star (boron not allowed to react but does participate as a heat sink) temperature calculations have been made and indicate that good afterburning potential exists with this solid fuel and with either liquid oxidizer considered. The combustion characteristics of the selected fuel will be further evaluated in subscale (4- to 6-inch diameter) and in full-scale (15-inch diameter) motor tests.

(U) The ignition and combustion characteristics of the hybrid gas generator exhaust stream, when mixed with air, will be determined in the direct-connect tests. These tests will be made using an afterburner ducted-rocket configuration and operating conditions that are similar to those used in other Air Force-sponsored programs. Thus, a direct comparison can be made between the performance of this hybrid system and the performance of ducted rockets using both solid propellant and slurry bipropellant gas generators.

(U) No reports have been published to date under this program.

(U) Advanced Maneuvering Propulsion Technology/Rocketdyne/R. Morin/ F04611-67-C-0116/R. L. Wiswell (RPRES)

(C) This effort is a two-phase program to provide for the feasibility demonstration of advanced space-maneuvering propulsion technology with the high-energy propellants, liquid fluorine and liquid hydrogen.

(C) The 24-month Phase I effort, which began 1 November 1967, will evaluate the critical technologies associated with the engine system and provide analysis and design of the complete propulsion system. Phase I has three tasks: Task I, Engine System Design and Analysis; Task II, Engine Critical Component Demonstration Testing; and Task III, Propellant Feed System Design and Analysis.

(C) Upon successful completion of Phase I, Phase II will be initiated and performed as one of two options. The first option provides for fabrication of an advanced flight-type propellant feed system and a flight-type advanced space-maneuvering engine, with the various propulsion components assembled into a breadboard configuration. Performance characteristics will be demonstrated through sea-level and simulated-altitude tests over a variety of selected mission duty cycles. This option encompasses 36 months. The second option provides for fabrication of only the flight-type advanced space-maneuvering F_2/H_2 engine with a comprehensive performance and durability test program conducted at simulated altitude conditions. This option requires 32 months.

(C) The Advanced Maneuvering Propulsion System (AMPS) concept with basic design parameters is illustrated in Figures 1 and 2. The engine configuration utilizes concentric thrust chambers; the outer main thrust chamber of 30,000 pounds thrust incorporates the toroidal-aerodynamic spike concept, the inner secondary thrust chamber of 3,300 pounds thrust is of a bell type. The thrust chambers are fed from independent turbopumps and each can be throttled over a 9:1 thrust range giving the engine

system an overall throttle ratio of 81:1. The normal mode of operation is for the thrust chambers to fire singularly; however, both chambers can be fired simultaneously. The propellant feed system consists of the main propellant tankage; thermal conditioning and support structures; zero gravity expulsion system; fill, vent, feed, and drain lines; propellant management system and a pressurization system.

Task I - Engine System Design and Analysis

(C) An analysis was completed to select the turbine drive cycles for the main and secondary engines, which resulted in hot hydrogen tapoff being selected for the main aerospike engine, and thrust chamber tapoff being selected for the secondary bell engine. As a part of the basic engine design parameter definition effort, an analysis of the major considerations influencing the selection of the nominal engine design mixture ratio and the propellant tank design mixture ratio was conducted. This analysis resulted in establishing the engine nominal mixture ratio at 12:1.

Task II - Engine Critical Component Demonstration Testing

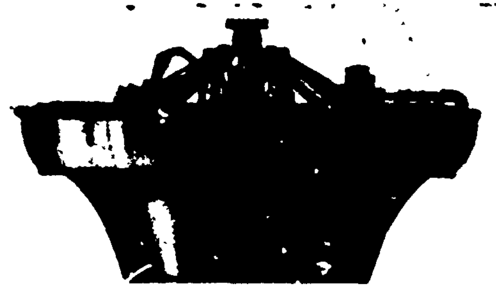
(C) The main thrust chamber design and development approach underwent a detailed reevaluation resulting in a change from the original subsonic nonstructural baffle approach to a supersonic structural baffle approach with complete chamber segmentation. Initial performance testing will be conducted with solid-wall 5-inch segments of the toroidal combustion chamber. The next level of testing will be done with 30-degree segments, both solid- and tube-wall configunations. The 30-degree segments will then be mated for 60-degree segment tests. The final performance demonstration will be conducted with a complete thrust chamber firing at simulated altitude condition.

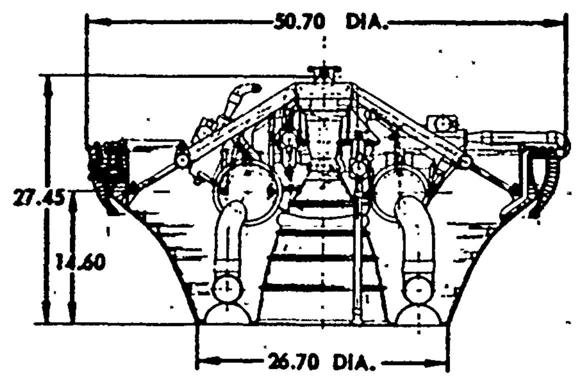
(C) All design has been completed on the 5-inch-segment hardware, and fabrication is in progress. The design of the 30-degree solid-wall and tube-wall segments is in progress.

Task III - Propellant Feed System Analysis and Design

(U) This is a competitive design effort between two subcontractors: Lockheed Missiles and Space Company and General Dynamics/Convair. One of them will be selected to do the propellant subsystem effort of Phase II.

(U) The effects of the thermal and space environments on the propulsion system have been defined. Data on these environments will be used in the other tasks so that the effects of the environments on the propulsion system and component designs, operations, and performance can be evaluated. Thermal conditioning system and tankage system analyses and designs are in progress.

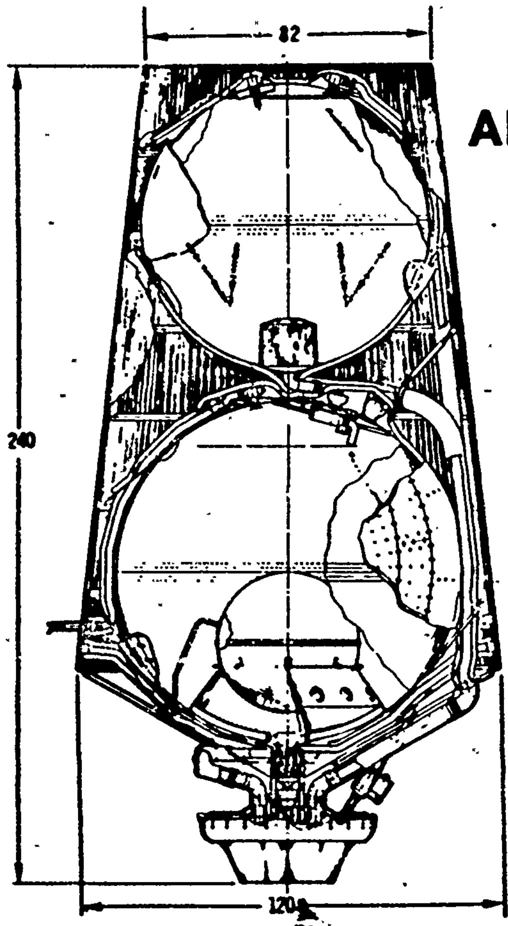




	MAIN ENGINE	SECONDARY ENGINE
THRUST, LB	30,000	3,330
CHAMBER PRESSURE, PSIA	650	750
VACUUM SPECIFIC IMPULSE, SEC	460	457.5
MIXTURE RATIO, O/F	12:1	12:1
THROTTLE RATIO	9:1	9:1
AREA RATIO	60:1	60:1
PRESENT DRY WT., LB (EST)	470	103
ULTIMATE DRY WT., LB (EST)	385	83

Figure 1. Advanced Maneuvering Propulsion System (Engine System Characteristics)

ADVANCED MANEUVERING PROPULSION SYSTEM (AMPS)



PROPELLANTS	LF_2 / LH_2
PROPULSION SYSTEM WEIGHT, LB	18,000
MAXIMUM THRUST, LB	30,000
THROTTLE RATIO	80:1
MIXTURE RATIO	12:1
GIMBAL ANGLE, DEGREES	±10
RESTART CAPABILITY (MINIMUM)	30
SPACE RESIDENCE TIME, DAYS	14
PAD HOLD CAPABILITY (NO F_2 LOSS)	INDEFINITE
LAUNCH VEHICLE	TITAN III-C

Figure 2. Advanced Maneuvering Propulsion System (AMPS)

(U) Air Force Reusable Rocket Engine Program/Pratt and Whitney Aircraft, Division of United Aircraft Corporation/R. R. Atherton/ F04611-68-C-0002/Capt E. D. Braunschweig (RPREB)

(U) This contract is the second phase of a two-phase program to demonstrate a high-performance, throttlable, reusable LO_2/LH_2 rocket engine. The purpose of this effort is to design, fabricate and test a lightweight, high-pressure, staged-combustion demonstrator engine with the characteristics given in Table I.

(U) The program began on 6 November 1967 and consists of a design support task, 10 component development tasks, an engine demonstration task and a flight engine design task. The design support task will permit modification and further testing of Phase I hardware to provide design inputs for the component development tasks. The major engine components to be developed are: Preburner Injector, Mainburner Injector, Nozzle, Mainburner, Cooled Thrust Chamber, Transition Case, Fuel Turbopump, Oxidizer Turbopump, Fuel Low-Speed Inducer, Oxidizer Low-Speed Inducer and Control System. In the engine demonstration task, the developed components will be assembled into a compact, lightweight demonstrator engine. Testing to demonstrate the characteristics of Table I will be performed. Preliminary designs of a flight engine that would result from an engineering development program will be established during the flight engine design task.

(C) (U) Design Support Task

(C) During the period from 6 November through 31 December 1967, preliminary designs for a fixed-area preburner injector were established. The selected configuration consists of 250 dual-orifice, tangential-swirler oxidizer elements each surrounded by a concentric fuel annulus. Detailed design, fabrication and testing of the injector to verify combustion performance and preburner temperature profile will be accomplished during the next report period.

(U) Preliminary designs for a modified roller-bearing tester were also studied during the report period. Final design and modification of the tester, procurement of test bearings and initiation of testing will be accomplished during the next report period. The test program will investigate the effect of roller length-diameter ratio (L/D), roller end clearance and negative radial clearance on bearing durability.

(U) Preliminary analysis and design efforts were initiated for the pump inlet evaluation, nozzle fabrication investigation, and controls component evaluation. During the next report period, design and fabrication will be completed and testing will be initiated in these areas.

(C) (U) TABLE I

DEMONSTRATOR ENGINE CHARACTERISTICS

Nominal Thrust	250,000 lb vacuum thrust with area ratio of 166:1 244,000 lb vacuum thrust with area ratio of 75:1 209,000 lb sea-level thrust with area ratio of 35:1
Minimum Delivered Specific Impulse Efficiency	96% of theoretical shifting Isp at nominal thrust; 94% of theoretical shifting Isp during throttling
Throttling Range	Continuous from 100% to 20% of nominal thrust over the mixture ratio range
Overall Mixture Ratio Range	Engine operation from 5.0:1 to 7.0:1
Rated Chamber Pressure	2740 psia
Engine Weight (with 75:1 nozzle)	3520 lb (with flight-type actuators and engine command unit) 3380 lb (less flight-type actuators and engine command unit)
Expansion Ratio	Two-position booster-type nozzle with area ratios of 35:1 and 75:1
Durability	10 hours time between overhauls, 100 reuses, 300 starts, 300 thermal cycles, 10,000 valve cycles
Single Continuous Run Duration	Capability from 10 seconds to 600 seconds
Engine Starts	Multiple restart at sea level or altitude
Thrust Vector Control	Amplitude: ±7 deg; Rate: 30 deg/sec; Acceleration: 30 rad/sec^2
Control Capability	±3% accuracy in thrust and mixture ratio at nominal thrust Excursions from extreme to extreme in thrust and mixture ratio within 5 sec
Propellant Conditions	LO_2: 16 ft NPSH from 1 atmosphere boiling temperature to 180°R LH_2: 60 ft NPSH from 1 atmosphere boiling temperature to 45°R

(C) (U) TABLE I (Cont'd)

DEMONSTRATOR ENGINE CHARACTERISTICS

Environmental Conditions	Sea level to vacuum conditions Combined acceleration: 10 g's axial with 2 g's transverse, 6.5 g's axial with 3 g's transverse, 3 g's axial with 6 g's transverse

(U) Throttling and Scaling Study for Advanced Storable Engine (ARES)/ Aerojet-General Corporation, Sacramento, California/J.A. Gibb/ F04611-68-C-0008/C.D. Penn (RPRA)

(U) ARES (Advanced Rocket Engine - Storable) is a staged-combustion rocket engine which operates with the storable propellant combination N_2O_4/50% N_2H_4 - 50% UDMH. The component technology required for this engine is being obtained on an Advanced Development Program, Contract AF 04(611)-10830, which is discussed elsewhere in this report. The effort on that program has been oriented toward a 100,000-lb fixed-thrust engine which would have prime application to a ballistic missile or space launch vehicle. In order to explore other potential applications, parametric data were needed to allow scaling to other thrust sizes and the throttling capability of the engine required evaluation. This study, which was recently completed, has provided this data.

(U) A computer simulation showed that the ARES staged-combustion cycle was adaptable to throttling and that a cycle power balance could be obtained at throttle ratios as low as 10:1. It was also shown that only one control valve would be required, this being a fuel control valve for the primary combustor. Throttlable engine designs were then established for thrust levels of 25,000, 100,000 and 500,000 lbs. The 25,000- and 100,000-lb-thrust engines have a 10:1 throttling range, and the 500,000-lb-thrust engine has a 5:1 throttling range. All the engines have unlimited restart capability and are capable of long-term standby in space.

(C) Some representative design point data are given below:

Design thrust, lbf	25,000 (vac)		100,000 (s.l.)		500,000 (s.l.)	
Nozzle Area Ratio	50	150	50	150	50	150
Thrust, Vacuum, lbf	24,200	25,000	111,065	115,250	582,200	604,100
Isp Vac., sec	314.5	324.6	316.5	328.4	316.5	328.4
Isp Efficiency, %	91.1	90.3	91.7	91.2	91.7	91.2
Pc, psia	2,800	2,800	2,800	2,800	2,800	2,800
Weight Dry, lb	207	209	869	883	6,110	6,130
Weight Wet, lb	215	217	933	946	6,811	6,828
Length, Overall, in.	43.2	59.5	48.3	119.3	179.7	260.1
Diameter, Nozzle Exit, in.	17.2	29.8	36.8	63.9	84.5	146.3

(U) Based on these point designs, scaling parameters were established over a thrust range of 25,000 to 500,000 lbs. These include engine weight, envelope, and delivered specific impulse. Development and production costs were also estimated as a function of thrust size.

REFERENCE

AFRPL-TR-68-2, "Throttling and Scaling Study for Advanced Storable Engine", Final Report, February 1968.

(U) Packaged Liquid Propellant Rocket Propulsion Technology for Air-Launched Missiles/Naval Weapons Center/L. Krzycki/MIPR AFRPL 7-10/B. Bornhorst (RPRRC)

(U) This effort represents 3 tasks of a 14-task project being conducted at the Naval Weapons Center as a oint Navy-Air Force Program for Packaged Liquid Rocket Propulsion. The objective of these three tasks is to establish operating criteria for increasing the performance of rocket propulsion systems in tactical missile applications using interhalogen oxidizer and mixed hydrazine fuel propellant combinations. Tasks supported by Navy funds principally pursue gel propellant technology; Air Force participation provides concurrent development of propulsion technology for advanced neat propellants. The ClF_5/MHF-5 propellant combination is used.

(U) Three approaches are being pursued. Positive expulsion of propellants from tapered tanks by means of rolling metal diaphragms is being evaluated. Chlorine trifluoride will be used as the propellant and a monopropellant hydrazine decomposition gas generator as the pressurization source. High chamber pressure performance (up to 2000 psi Pc) of the ClF_5/MHF-5 propellant combination will be evaluated. This evaluation will be performed in ablative chambers rated at 2000-lb thrust which were demonstrated in previous test series using CTF and MHF-3 under similar operating conditions. The test duration objective is 50 seconds. Throttling techniques will be evaluated with the ClF_5/MHF-5 propellant combination. The performance of momentum exchange and variable orifice pintle injectors will be evaluated in ablative chambers similar to those used in the previous task. A throttling range of at least 7:1 from 1500 psi to approximately 250 psi chamber pressure will be demonstrated.

(U) Tapered inserts for 12-inch nominal diameter tanks and tapered diaphragms are being fabricated. A 6° taper is being used for the initial evaluation. High chamber pressure testing has been initiated using a

prototype injector and heat-sink chamber assembly for short-duration checkout tests to establish operating parameters. Components for the 50-second tests are being fabricated and assembled. Three designs of a momentum exchange injector are being fabricated for evaluation. Selection of the variable-area orifice injector has not been settled.

(U) Pulse Motor Combustion Instability Investigation/Project 305804BRF/
Lt J. Kiselyk (RPRRC)

(U) The pulse motor program was originally established to investigate the combustion stability characteristics of various propellant combinations and injector patterns. Currently, a combustion correlation support task, a rating technique effort, and a stability comparison between the fuels N_2H_4 and MMH used with the oxidizer N_2O_4 are being performed. The effort for the next 6 months will be primarily directed toward determining the stability characteristics of the storable fluorinated propellants, Compound "A" and Chlorine Trifluoride, in combination with hydrazine blends. Testing is conducted with either a 12.8-inch or a 15-inch-diameter engine with a flat-face injector composed of six or eight injector spuds (containing the injection pattern of interest) which are mounted around the periphery of the injector face. Pulse guns discharge into the chamber creating disturbances that are monitored with high-frequency pressure transducers. The data gained is used for relative stability evaluation of various injection patterns and propellants.

(U) Combustion Correlation Support: This task is in support of the in-house combustion correlation program. The overall objective of the task was to determine what degree of combustion stability correlation exists between two engines of the same physical size: one with a full-face injection pattern, the other with reduced propellant flow through the same pattern, but limited to the area of the pulse motor injector spuds. This effort has been accomplished and the test results are being utilized by the Combustion Correlation Program (see Program No. 305804BRH).

(U) The N_2H_4/MMH Stability Comparison Study: This study seeks to offer guidelines on the relative stability of the propellant combinations N_2O_4/N_2H_4 and N_2O_4/MMH as well as identifying any potential problems in the use of these propellants. This work is in support of the "PBPS"

effort. In an attempt to cover a broad base, three injection patterns were tested: a like-on-like doublet; an ox-fuel-ox triplet; and a triplet fan. The triplet fan is a group of ox-fuel-ox triplets composed of fans formed by like-on-like doublets resulting in a finely atomized spray. Tests were conducted at the optimum mixture ratio as well as at low mixture ratios in an attempt to simulate a film-cooled environment. The N_2O_4/N_2H_4 propellant combination displayed poorer stability characteristics than N_2O_4/MMH. This broad trend was particularly noticed at lower mixture ratios. In one such case a sizable "pop" occurred driving the system unstable. In addition, a theoretical combustion stability model is being used to analyze the test data. This model was developed by Dr. Priem of NASA and extended by Dynamic Science Corporation under an Air Force contract.

(U) Pulse-Gun Repeatability Study: A limited pulse-gun repeatability study was conducted to determine the degree of data scatter inherent in pulsing the combustion process. This information is necessary in order to determine the relative stability of variations in injector design parameters and propellant combinations. The study indicates that considerable scatter ±25% of the mean pressure disturbance for a given gun size exists and that the shock wave emanating from the pulse gun is nearly spherical with its greatest strength in the direction the gun is pointed. It was also determined, because of the directional nature of the pulse gun, that the relative position of the pulse gun to the pressure transducer is important in analyzing stability data.

(U) The following reports have been published under this program:

1. AFRPL-TR-66-130, AD 802488, "Investigation of Hybaline A_{14} as a Combustion Instability Suppressant in a LO_2/RP-1 Combustion System", June 1966, unclassified, in-house, RPRRC, 305804BRF.

2. AFRPL-TM-65-31, "An Experimental Combustion Evaluation of Hydrazine-Type Fuels with the N_2O_4 Oxidizer", July 1965, unclassified, in-house, RPRRC, 305804BRF.

3. AIAA Paper No. 67-474, "Influence of Storable Propellant Liquid Rocket Design Parameters on Combustion Instability", July 1967, unclassified, in-house, RPRRC, 305804BRF.

(U) Spray Analysis Investigation/Project 305804BRG/Lt W.B. Kuykendal (RPRRC)

(U) The objective of this project is to obtain injector droplet size, mass distribution, and mixture ratio distribution data for analysis in a theoretical combustion instability model and correlation with hot-firing data from other in-house combustion technology programs. An additional objective of this program is to relate droplet size distributions to generalized injector design parameters and propellant properties.

a. (U) Spray Mass and Mixture Ratio Testing: Fourteen tests were conducted in support of the Combustion Correlation Program, the High-Chamber-Pressure Combustion Dynamics Program, and Project Flintstone. Data from these tests was imput to a computer program which yields mass and mixture-ratio data across the injector face. In addition the 50,000-lb thrust cold-flow facility has been improved by the installation of air-operated shutters which provide a uniform sample across the injector, and simplify test operation.

b. (U) Propellant Properties Study: A test program of 22 photographic runs varying the propellant physical properties of density, surface tension, and viscosity in addition to varying orifice diameter and injection velocity has been completed. Two spuds were fabricated to yield three like-impinging doublets with an L/D of 10 or more.

(U) In order to vary the physical properties the simulants tabulated below were used:

Simulant	Specific Gravity	(Centipoise) Viscosity	Surface Tension (Dynes/cm)
Water	1.00	1.00	73
Trichloroethylene	1.46	0.58	32
1, 2 Dibromoethane	2.17	1.72	39
Glycerin and H_2O	1.1 to 1.17	2.57 to 14.66	36 to 59
Zonal A and H_2O	1.00	0.96	26
Alkonol B and H_2O	1.00 to 1.02	1.02 to 1.31	31 to 29

By proper selection of these simulants it was possible to simulate a range of propellant properties.

(U) Data reduction is in progress and the complete findings will be published in the form of a technical report.

c. (U) Injector Parameters Study: Design and fabrication of a variable-element injector have been completed. A test program has been established which will allow for the investigation of various injector design parameters on droplet size. Testing will begin during the early part of the next report period.

(U) A paper entitled "Influence of Storable Propellant Liquid Rocket Design Parameters on Combustion Instability" was presented at the AIAA Propulsion Joint Specialist Conference in July 1967. No other reports were published during this period.

(U) Combustion Correlation Program/Project 305804BRH/Capt J. F. Ensminger (RPRRC)

(U) The objective of this program is to investigate and evaluate the correlation of the AFRPL combustion tool (pulse motor) with full-scale assemblies in order to determine its usefulness and/or limits of applicability. In the process, a potentially more flexible combustion tool, the spud motor, is to be designed and evaluated. An additional objective is to demonstrate the effective use of acoustic liners for suppressing instabilities in larger scale, high-thrust rocket motor assemblies.

(U) Hot firings were conducted with four different injector patterns using N_2O_4/Aerozine-50 and N_2O_4/MMH as propellants at chamber pressures of 300 and 600 psia. Two instability-inducing devices (pulse guns and non-directional bombs) were used. The correlation between the full-scale motors and the combustion tools will be made by comparing the following parameters: (1) the perturbation magnitude required to drive the system unstable; (2) the time for a pressure disturbance to damp out; (3) peak resultant pressure perturbation; (4) the instability modes and frequencies; and (5) combustion efficiency (C*). The spud motor concept has been tested by plugging orifices of the full-scale injectors to simulate the actual spud motor patterns. The effectiveness of acoustic liners has been tested using the same injector and nozzle hardware (only three injector patterns) and data analysis technique described above. An uncooled liner sleeve mated to a redesigned thrust chamber section was used for this evaluation.

(U) All the tests have been completed and the final reports are being prepared. The triplet and the triplet fan injector patterns were spontaneously unstable. The doublet injector pattern was spontaneous instability but most tests with the pulse motor were more stable. Preliminary conclusions are that (1) the pulse motor is not an absolute stability-evaluation device, but is useful for screening injector patterns and

(2) the spud motor does show a better correlation with full-scale engine stability behavior than the pulse motor. The acoustic liner was totally successful with the doublet pattern and yet showed only very slight success with the triplet patterns. Tests using a state-of-the-art designed full-length liner with the triplet Mod 1 pattern did not damp out the spontaneous instability operating at Pc = 300 psia. Subsequent analytical study revealed that this effect could be due to the high chamber velocity ($\simeq$ 1600 ft/sec) present in the relatively low-contraction-ratio (1.56) engine; the liner's calculated absorption is less than $\frac{1}{2}$ of 1% under these conditions. Analytical studies show that by increasing the contraction ratio to 3.20 (i.e., Pc = 600 psia), at the same propellant flow rate, the chamber gas velocity drops to 800 ft/sec and the liner has good absorption. Tests conducted using the liner at Pc = 600 psia stabilized the spontaneous instability as well as damped out various pulse-gun disturbances. Another pattern, a self-impinging doublet, has been fired using the same liner at identical operating conditions. During baseline stability tests (no liner) this pattern was spontaneously stable but could be driven unstable by relatively small pulse-gun charges, 10 to 15 grains. The first liner tests were conducted at a low (800 ft/sec, Pc = 600 psi) chamber velocity where the liner should be effective. This, indeed, was the case and the liner damped out pulse-gun disturbances up to 80 grains in less than 30 msec. The liner was then tested at a chamber pressure of 300 psi, velocity of 1600 ft/sec, in expectation that the liner would not be effective. But this was not the case, the liner damped out 80-grain charges as well as in the 800 ft/sec case. The difference between the chamber gas acceleration for the various injector patterns explains why the liner was successful in the case of the doublet, but not with the two triplet patterns. The two triplets, with direct unlike impingement, attain high velocities very close to the injector face, thus decreasing the liner's absorption within this sensitive zone.

(U) A paper entitled "Combustion Chamber Velocity Effects on Acoustic Liners" was presented at the Fourth ICRPG Combustion Conference, 2-13 October 1967 at Stanford Research Institute, Menlo Park, Calif.

IN-HOUSE LABORATORY PROGRAM

(U) High-Chamber-Pressure Combustion Dynamics/Project 305804BRI/ T. J. Fanciullo (RPRRC)

(U) The High-Chamber-Pressure Combustion Dynamics Program was designed to investigate the combustion properties of oxidizer-rich, high-chamber-pressure, preburner (or gas generator) combustors utilizing storable N_2O_4 and Aerozine 50 as propellants. The preburner is used to drive the turbine which provides the power for turbopumps of rocket engines employing the staged-combustion topping-cycle design. The gases of the preburner, after passing through the turbine, enter directly into a second chamber in which the rest of the fuel is introduced. Thus all the gases developed from the propellants are used as thrust.

(C) During the past 6 months, several candidate injector designs were tested and evaluated for performance and combustion stability. The nominal chamber operating pressure of these injector assemblies was 3500 psia. The nominal thrust produced was 15,000 lbf. The mixture ratio was varied from 8:1 to 16:1 with 11.5:1 being the nominal case. Two basic combustors were utilized. One was a conventional cylindrical shape and the other was annular in construction. Three injector designs were tried. The first one was a cylindrically shaped full-face or tran-spray type, in which all the oxidizer passed through a rigimesh (screen type) material and the fuel was introduced through 19 spray swirler jets laid out in concentric circle arrays on the injector face. The second injector was also a cylindrical type but employed concentric arrays of four oxidizer jets impinging on one central spray swirler fuel jet. The remaining injector type was designed for an annular combustor and was also a full-face or transpray type, but with the modification of an additional 448 small-diameter oxidizer showerhead jets laid out in concentric arrays around 19 fuel spray swirler jets.

(C) The cylindrical transpray injector proved to be the most stable, combustion wise. An 80-grain pressure pulse inducer gun was used to introduce a nonlinear pressure spike. Induced overpressures greater

than 170% of chamber pressure failed to trigger an instability. Greater stability was observed with a shorter combustion chamber. It was also noted that the (8:1 to 10:1) lower mixture ratios were more stable than the higher (10:1 to 16:1) mixture ratios.

(C) The annular transpray injector proved to be marginally stable. A small, low-frequency pressure spike (22% of chamber pressure) produced a spontaneous instability corresponding to the first tangential acoustic mode. Subsequent tests will be made to investigate this stability condition, as the design is attractive as far as packaging is concerned.

(C) The cylindrical quadlet injector assembly proved also to be marginally stable, with a serious injector-chamber compatibility problem. To cure this problem film coolant was added. However, the amount at first was not sufficient to protect the chamber, so the amount was doubled. This amount, approximately 13% of the total oxidizer flow, provided a good barrier on the wall and improved the stability sufficiently enough to withstand repeated 120% (of chamber pressure) overpressures without going unstable.

(C) The performance of these injector assemblies, (although not important for gas generators) ranged from 77% to 86% of theoretical characteristic exhaust velocity. The reason the percentage is not higher is because these combustors are operated at higher than optimum mixture ratios to provide low-enough flame temperatures which are compatible with the pump turbines.

(U) This program is in the middle of its test phase and no technical reports have been written. The scheduled final report for the preburner development work is March 1968.

(U) Compound A (ClF_5) Propulsion Technology Program/Project 305808D-RL/Lt D.A. Shantz (RPREA)

(U) The overall objective of this program is to demonstrate technology for a flight-type attitude-control engine, which will utilize the MMH/ClF_5 propellant combination. This propellant combination can provide significant improvements over current combinations being used for attitude control. The system can produce a higher density impulse, both propellants have low freezing points (i.e., more compatible with space environments), and MMH/ClF_5 exhibits very desirable ignition characteristics. The project was originally a phase of the Attitude Control Evaluation Project, however, it was initiated as an independent program in July 1967. It is anticipated that the project will run for 24 months.

(U) The program will be conducted in two phases. In Phase I, various injector/thrust chamber configurations will be tested to determine the best combination. All tests conducted during this phase will be run at ambient conditions. After the best injector/thrust chamber has been chosen, it will be modified to a flight-type configuration and tested, at simulated altitude, during Phase II of the program.

(U) Phase I Progress: The sea-level facility which will be used for this phase of the program is 90% complete. As soon as a ClF_5 disposal unit is installed in the test cell, the first test engine will be installed and the system will be ready for checkout. Initiation of testing is expected during the latter part of February 1968.

(U) Phase II Progress: The design of the altitude facility to be used during this phase is complete. Fabrication and installation of this facility has been contracted and will begin early in January 1968. Altitude tests of a flight-type engine are scheduled to be initiated in December 1968.

(U) Attitude-Control Evaluation (ACE)/Project 305808D-RO/
K.O. Rimer (RPREA)

(U) The Attitude-Control Evaluation program is a long-term project directed toward achievement of fundamental understanding of the performance, reliability and accuracy characteristics of bipropellant attitude-control engines. The ultimate objective is the modeling of these features by suitable computer programs which will permit accurate prediction of attitude-control engine behavior from design information and a small sample of test data. Such a capability would be of great utility in minimizing the cost of development, qualification and acceptance testing, and would permit a significant improvement in specifications for bipropellant attitude-control systems.

(U) Before actual engine testing toward the above objective could be started, new instrumentation and data-processing techniques had to be developed. The first phase of these developments was completed in November 1966 with activation of a test facility capable of measurement of single pulse performance parameters for pulse width down to .01 seconds. Nine fully developed attitude-control engine types were scheduled for testing to provide the first data sample for analysis, and determination of the design parameters of major influence on engine characteristics. One of these engines completed the full standard test matrix and a second was partly tested when SAMSO requested that the facility be made available to support the development of attitude-control systems for MOL. Testing toward achievement of the ACE program's objective was interrupted in February 1967 and the facility has been continuously utilized since then in support of MOL. The facility will be fully utilized in support of two additional SAMSO projects throughout 1968.

(U) This time is being utilized to develop further improved instruments and data-processing techniques, and to conduct investigations into the elemental processes which make up an attitude-control engine pulse.

Under contract, a highly accurate model of the ignition process has been developed and experimentally confirmed. An in-house effort is currently under way to couple this ignition model with the manifold fill dynamics and extend its applicability to a wide range of propellants. These instrumentation developments and elemental process investigations are covered in the Project 3850 and Project 3148 sections of this report, respectively.

(U) It is currently planned to resume testing toward the ACE objectives in January 1969. Although the systems support programs have delayed achievement of our ultimate objective, the improved instrumentation and fundamental understanding of elemental processes should greatly improve the utility of our attitude-control engine pulse-mode performance model.

(U) Tube Connector Development/Project 305803ERB/Capt G. N. Graves (RPRPD).

(U) The objective of this project is to evaluate performance, service and operational problems, and skill level requirements for tubing systems technology for mechanical, welded, and brazed connectors in both the laboratory and field.

(U) This work is being accomplished by testing tubing connectors in stressed environments typical of those encountered in rocket propulsion systems while monitoring for leakage or structural failure. Presently used connectors have been tested to obtain a baseline for comparison to AFRPL contractor-developed fittings and other advanced fittings. Weld tooling is being evaluated for in-the-field fabrication and repair by use in fabricating sections of the Phase II Tank Storability Program, Project 305805FRJ. Stressed coupons are being used to test compatibility of various gold-nickel and silver-copper braze alloys with N_2O_4. The braze alloy composed of 72% silver-28% copper was found to be unacceptable for use in N_2O_4 even in the unstressed condition.

(U) Baseline data were generated on plain tubing sections and AN flared connectors. Eighty standard AN flared connectors were used in 52 tests. Approximately one-third leaked upon initial assembly. The remaining connectors generally sealed in the 10^{-8} to 10^{-6} standard cubic centimeter/second range. A separate report on the flared-connector testing is being prepared.

(U) One hundred and fifty axial-load, torque, and deflection-rate tests were also conducted on fluid connectors to obtain data for use in the Battelle Memorial Institute developed performance-prediction procedure. The results of the performance prediction and experimental performance will be compared in two reports due for completion in January 1968.

(U) An advanced connector called the AFRPL connector, developed by Battelle Memorial Institute for the Air Force Rocket Propulsion Laboratory, has been tested in proof and burst pressure, repeated assembly tests, and stress reversal bending. With over 150 seals tested in the 1/4, 3/8, and 1/2 tube sizes, no connector has leaked at a rate greater than 7×10^{-7} cubic centimeters per second (2 cc per year). The mean measured leakage of all AFRPL connectors was 3.5×10^{-8} atm cc/sec. This correlates well with the 2.6×10^{-8} atm cc/sec mean leakage rate reported by Battelle.

(U) The Tube Connector Development Program will continue during the next 6 months with further evaluation of the AFRPL onnector and commercial connectors, welded fittings, and brazed fittings stress corrosion tests.

REFERENCES

1. "Development of AFRPL Threaded Fittings for Rocket Fluid Systems", AFRPL-TR-65-162; Goobich, B.; Adam, J.W.; Baum J.V.; and Trainer, T.M.; Battelle Memorial Institute, Columbus, Ohio, November 1965, AD 474789.

2. "Exploratory Development Work on Families of Welded Fittings for Rocket Fluid Systems, Final Report"; AFRPL-TR-65-161; Padian, W.D.; Lambase, J.M.; and Robelotto, R.P.; Los Angeles Division, North American Aviation, Los Angeles, Calif., October 1965, AD 475030.

(U) Liquid Propellant Expulsion Technology/Project 305805ERD/
Lt R.B. Mears (RPRPT)

(U) The first objective of this program is to evaluate bladders and screens for storable propellants in direct support of Program 922. A requirement exists for expulsion bladder materials that can withstand a large number of propellant expulsion cycles. Rubber expulsion bladders will be tested to determine whether Ethylene Propylene Rubber (EPR) and Carboxy Nitroso Rubber (CNR) have characteristics superior to other materials used in expulsion bladders.

(U) The use of surface tension devices for space vehicles which require a restart capability and/or have a problem controlling the center of gravity of the vehicle is being considered for advanced systems. Test data is required on the capability of screens to orient both storables and cryogens The compatibility of screens with toxic propellants and their heat-transfer characteristics with cryogens are two fields where data is especially needed before assignment to advanced systems can be made.

(U) There have been no significant results obtained yet since the program is in the buildup phase.

(U) Cryogenic Propellant Storability In Space/Project 305806ERN/
Lt T.J. Kelly (RPRPP)

(U) The objective of this program is to evaluate the performance of cryogenic propellant systems in a simulated space environment and to provide experimental test data for cryogenic storability computer program AF 04(611)-10750.

(U) The first phase checkout test has been completed and is documented in AFRPL Technical Report 66-31. The remaining phases of the program have been renumbered consecutively II-V. The second phase has just entered the test portion of the program. A lengthy delay was encountered due to various leak problems attributed to the storage of a cryogenic (liquid hydrogen) under vacuum conditions in a complicated test system. The problems have been solved and just prior to this writing, two successful expulsion tests were conducted but the data have not been reduced. These tests used cold helium gas ($-423^{o}F$) at 50 psia to expel both tanks, LN_2 and LH_2 separately. Very shortly, testing will be continued using hot gases at various temperatures and pressures for the programmed expulsions. The results of these tests should verify analytical work done under Contract AF 04(611)-10750 with McDonnell Douglas Corporation, managed by G. W. Burge. The areas investigated by this work are pressurization systems, stop-start operation and feed system and venting losses. One unique factor also to be evaluated through storability tests is that the superinsulation applied to the Phase II test article is applied on the shroud of the system and not directly to the tank. During all phases of this program, LN_2 is being used to simulate LF_2. Phase III of this program will subject an 8-foot superinsulated LH_2 tank to a simulated space environment to determine how the tank-mounted insulation on it compares to the shroud-mounted concept used on the previous phase. This test article was modified, insulated, and instrumented under Contract F04611-67-C-0015 with McDonnell Douglas. The system is built up and is currently awaiting test. The fourth phase of the program will examine

the feasibility of modifying the existing Centaur vehicle and thus give it a long-duration mission capability in space. The modification consists of cutting a section out of the vehicle and replacing it with an additional bulkhead. Superinsulation is then applied to the exterior surface. This test system has been delivered under Contract F04611-67-C-0004 with General Dynamics/Convair, and it also is awaiting test. The fifth and currently last phase of the program is concerned with investigating methods of maintaining a vent-free fluorine feed system. It also investigates the effects of each method on vehicle performance during conditions of ground hold, and the effects on operational flexibility while performing a military mission in space. This work is being handled under Contract F04611-67-C-0044 with Martin Marietta Corporation, which is currently in the 10th month of a 16-month contract.

REFERENCES

1. "System Effects on Propellant Storability and Vehicle Performance", AFRPL-TR-66-258, AD 802590.

2. "Tank-Mounted Insulation Program", Final Report AFRPL-TR-67-161, May 1967, AD 817357.

3. "Partitioned Centaur Test Tank", AFRPL-TR-67-160, May 1967, AD 817380.

4. "Vent-Free Fluorine Feed System," Final Report AFRPL-TR-67-323, Vol I, March 1968.

(U) Thrust Chamber Technology Program (Flintstone)/Project 305803FRC/ Lt G.O. Beris (RPRRC)

(U) The objective of this program is to evaluate materials and design concepts for passively cooled thrust chamber assemblies for future high-energy liquid propellant rockets. To accomplish this, material inserts, nozzles, thrust chambers, and thrust chamber assemblies are procured through contracts with industry, and tested in-house. Thrust chamber assemblies are also designed and built in-house for use as workhorse hardware.

(U) A small-scale test stand is being built at the 1-46A area for testing thrust chamber assemblies up to 600-lb thrust with either storable or fluorinated oxidizers.

(U) Major efforts now in progress include evaluation of free-standing pyrolytic graphite (PG) nozzles under contract with the Marquardt Corporation, and evaluation of composite PG throat inserts under contracts with Aerojet-General Corporation and Philco-Ford Corporation. The free-standing PG nozzles are being tested at 100 and 300 psia and 1000-lb thrust with the CTF/MMH propellant combination. Preliminary checkout tests with workhorse hardware are nearing completion.

(U) Evaluation of the composite PG inserts will be conducted after completion of the free-standing PG nozzles testing. Workhorse hardware to test the inserts has been procured on contract and is also being built in-house. Two injectors, three chambers, and one nozzle for use with CTF propellant have been obtained from Astrosystems International Inc. Checkout of the hardware is in progress. Primary and backup LF_2 injectors are also being fabricated in-house and will be used for the PG insert testing. Two inserts from Philco have been received and testing is expected to begin February or March 1968. The inserts to be tested with LF_2 will be at 200 psia and those with CTF at 300 psia. Thrust for all tests will be 3000 lb.

(U) The following reports have been published under this program:

1. AFRPL-TM-64-11, "Throttling Tests with STL Throttling Injector," February 1964.

2. AFRPL-TM-64-29, "Testing of Uncooled Thrust Chambers with Propellants LF_2/N_2H_4 Blend," September 1964.

3. AFRPL-TR-65-101, "AFRPL Liquid Fluorine Rocket Nozzle Test Facility," March 1965, AD 470153.

4. AFRPL-TM-66-32, "Development of Electroformed Water-cooled Thrust Chamber Assemblies," December 1966.

(U) Packaged System Storability/Project 305805FRJ/Maj R.B. Tanner (RPRPT)

(U) This project was formerly 675305123, Liquid Propellant Tank Storability Evaluation.

(U) The objective of this program is to evaluate current materials and processes for the fabrication of storable propellant tankage and to demonstrate the storability of propellant tankage and feed systems in extended contact with stored propellant and while under adverse environmental conditions. This is to be accomplished by an environment of 85°F and 85% humidity for periods of up to 5 years. Determination of leakage and degradation of material strength, propellant composition, and component functional reliability will be accomplished. The project is structured in the following phases of testing:

(U) Phase I: Small Containers - One hundred and five small containers have been procured and are in test.

(U) Phase II: Twenty-four systems will be integrated and loaded with propellants at the AFRPL using both machine- and hand-welded tubing, AFRPL mechanical fitting technology and state-of-the-art componentry. Tankage materials are 2219-T91 aluminum and AM350 steel.

(U) Phase III: Twenty-four 15-gallon tanks fabricated from several aluminum stainless steel and titanium alloys are being evaluated for propellant containment in state-of-the-art tankage. Tanks will be filled with N_2O_4 and Compound A. Additional tankage will be procured for N_2O_4 and hydrazine testing.

(U) Phase IV: Several existing tanks fabricated under other programs will be filled with propellants and tested for storability.

(U) Phase V: Twenty-four prepackaged feed systems are in test. Each system consists of a loaded tank and expulsion system coupled to a charged pressurization subsystem.

(U) Phase I Progress: A leak was discovered in one of the small containers - Al 2014-T6, loaded with N_2O_4. The vessel was in test from 7 September 1966 to 4 December 1967.

(U) Phase II Progress: Hand-welding of the stainless steel tubing joints has been completed and aluminum hand-welding initiated. Approximately half the weld fabrication is complete.

(U) Phase III Progress: Seven 15-gallon tanks have failed, five with ClF_5 and two with N_2O_4.

(U) Phase IV Progress: The storage test of the Agena tank in support of the SAMSO Agena Improvement Program was completed 1 September 1967. The tank did not leak.

(U) Phase V Progress: Eighteen prepackaged systems are in test. Four additional prepackaged systems have been delivered and will be loaded with NASA Spec. N_2O_4 and put into test. One ClF_5 system was destroyed because of a propellant fill-tube leak.

REFERENCES

1. "Design and Manufacture of Fifteen-Gallon Propellant Vessels for Tank Storability Program" AFRPL-TR-66-35, March 1966, AD 480151.

2. "Design, Fabrication and Test of Small-scale Storable Propellant Vessels" AFRPL-TR-65-194, January 1966, AD 476248.

3. "Storability Demonstration Feed Systems", AFRPL-TR-67-252, October 1967, AD 822302.

(U) Transtage ACS Engine Evaluation (TRACE)/Project 624A00D-RT/ P. C. Erickson (RPREA)

(U) An evaluation of the final flight-configured Rocket Engine Assembly (REA) being developed by Rocket Research Corporation under contract to Martin Company, is being conducted at the request of SAMSO. The REA will replace the current bipropellant attitude-control engine on the Transtage, starting with vehicle 17.

(U) Testing of the monopropellant N_2H_4 REA will include:

a. Determination of performance under various operating conditions.

b. Contaminated catalyst bed.

c. Determination of spiking conditions.

d. Maximum injector soakback temperatures.

e. Simulated-mission duty cycles.

(U) All testing will be at simulated altitude conditions in T.S. 1-14, Cell C. Testing will begin shortly after delivery of the REA, currently scheduled for February 1968.

(U) ACS Monopropellant Exhaust Contamination Investigation/Project 624AOODRV/P.J. Martinkovic (RPRPP)

(U) The objective of the program is to investigate ACS Monopropellant (N_2H_4/Shell 405 catalyst) plume effects on spacecraft and satellite components associated with the Transtage vehicle.

(U) The program was initiated on 1 November 1967 and is divided into two phases as follows:

a. Investigate the plume effects on the Transtage vehicle radiator thermal-control coating paint relative to change in the initial ratio of absorptance and emissivity.

b. Investigate the ACS plume effects on on-board satellite space-borne equipment, i.e., solar cells and optics regarding deposition and physical damage to the equipment causing changes in system operational characteristics.

(U) Tests will be conducted under simulated altitude conditions (500,000 to 600,000 ft). Test duration under vacuum conditions will be from 15 to 38 days and engine pulse widths will vary from 50 milliseconds to 2 seconds.

(U) This is a 9-month effort and the results of this program will be published in August of 1968. However, monthly progress letters are being submitted to SAMSO/SMVTD/Lt D. Walker.

(U) MHD Gas Generator/Project 314527G-RW/C. T. Hurd (RPREP)

(U) AFAPL's Project Brilliant is a combined effort of five Air Force Laboratories and five contractors to provide increased capabilities for battlefield illumination by tactical and reconnaissance aircraft. The AFRPL will supply the gas generator.

(U) The AFRPL in-house effort, in support of battlefield illumination, is designed to provide the AFAPL with the initial LO_2/JP-4 combustor for an MHD power-generation system and to supply pertinent hardware-cooling and durability criteria. To meet the AFAPL-requested delivery dates of 1 November 1967 for the initial combustor and 1 March 1968 for an improved combustor, the Rocketdyne LR-101 Atlas vernier engine was selected to meet AFAPL-generated requirements.

(U) The engine required for use at the AEDC by November 1967 has been test-certified and delivered. The combustor's exhaust is seeded with potassium ions to 1% by weight of the total propellant weight flow. Ethyl alcohol saturated with potassium hydroxide is injected into the fuel-feed lines at a rate of 25% of the total fuel flow. The propellant weight flow can be varied from 3.75 to 4.25 lb/sec at mixture ratios up to 2.6. This mixture ratio is optimum to provide proper ionization temperatures with this seeding technique. Although theoretical calculations indicate that the gas exit pressure would be low, pressure measurements from actual combustor firings in an MHD simulation channel show it to be 75 psia, which is the required channel operating pressure. The initial combustor configuration was fired for a 5-min.-duration run, with no chamber damage and only slight throat erosion.

(U) The next phase of testing is to obtain the combustor's conductivity performance by simulation channel firings. The channel, consisting of 25 insulated electrodes with a diverging bore through its center, mates

to the combustor nozzle and has a 500-volt potential across the entire channel. When the combustor is firing, the voltage drop measured between each electrode indicates the conductivity of the ionized gas in the channel.

(U) Two approaches are being pursued to improve this combustor for a March 1968 delivery. A Rocketdyne experimental splash-plate injector appears capable of improving the combustor's durability at higher chamber pressures and longer durations. This new injector has also been tested at mixture ratios higher than that of the standard injector with less streaking in the chamber. To improve its seed rate from 1% to 4% of the total weight flow, a kerosene-soluble potassium compound, KTA, has been purchased. This new propellant will be tested in the channel to obtain conductivity data.

(U) Marquardt R-1E Thruster Evaluation/Project SSDTMCD-RE/
P.C. Erickson (RPREA)

(U) Testing of the Marquardt R-1E 22-lb thrust bipropellant engine was initiated in May 1967 at the request of SAMSO. This engine has been selected by McDonnell Douglas Corporation to be used on the attitude-control system of MOL. Characteristics of the engine, as published by the manufacturer, are shown in Table I. The AFRPL testing will provide a comprehensive evaluation of the pulse-mode performance capability of the engine. Facility and instrumentation systems to be used in the performance evaluation were developed for this specific purpose in another project, Project ACE, which has been temporarily suspended to permit the conduct of this test program.

(U) The test program consists of the following five phases:

I. Pulse Performance: Testing consists of firings at pulse widths ranging from 5 ms to 200 ms at nominal propellant temperatures and inlet pressures. Determination is made of pulse impulse, specific impulse and mixture ratio versus valve applied signal time (pulse width) and valve open time.

II. Inlet Pressure Variation: Testing consists of firings at pulse widths ranging from 10 ms to 100 ms, at all injector inlet pressure combinations of nominal pressure, nominal plus 10% and nominal minus 10%. Measurements are made to determine inlet pressure, impulse and specific impulse versus mixture ratio.

III. Engine Pulsing Life: Testing consists of firing to accumulate 50,000 pulses on one engine. Seventy percent of the pulses will be in the 0.15 to 0.35 lbf-sec impulse range with the remaining pulses distributed at pulse widths up to 130 ms. The majority of the firings are to be conducted with engine temperature at $20^{\circ}F$ to $200^{\circ}F$. Determination is made of the performance throughout the life test.

IV. Propellant Valve Voltage Variations: Testing consists of firing at pulse widths to produce impulses between 0.15 and 0.35 lbf-sec with valve voltage at nominal, nominal plus 3 volts and nominal minus 3 volts. Engine thrust chamber initial temperature, for each pulse, will be 20°F with injector temperature of 35°F. Determination will be made of specific impulse, impulse and mixture ratio versus pulse width.

V. Steady-State Performance: Testing consists of firings of 15-second duration at nominal conditions for a total firing time of 2000 seconds. Determination is made of specific impulse and inlet pressure versus mixture ratio as well as steady-state equilibrium and maximum hardware soakback temperatures.

(U) All testing is conducted at simulated altitude conditions of 100,000 ft or greater and with helium-saturated propellants.

(U) During the reporting period, considerable effort has been expended in modification of the test facility to accomodate the test plan. Design, fabrication and checkout of the helium saturation system, valve open timer, and temperature conditioning equipment were the major additions to the facility. Modifications were also made to existing data reduction programs to provide the required information and format.

(U) Engine testing has resulted in the completion of Phase I, II, and 20,000 pulses of the programmed 50,000 pulses of Phase III. Data is being analyzed and will be discussed in the next report. Completion of the testing is scheduled for February 1968 with final report completion in March 1968.

(U) During this period, effort was also expended in an evaluation of the accuracy of the digital data acquisition system and the data reduction computer program. The results of this evaluation will also be presented in the next report.

TABLE I

MARQUARDT R-1E THRUSTER CHARACTERISTICS

Thrust (Vacuum)	22 lbf
Propellants	N_2O_4/MMH
Propellant Inlet Pressures	200 psia
Mixture Ratio (O/F)	1.6
Propellant Flow Rates	Ox 0.048 lb/sec Fu 0.030 lb/sec
Chamber Pressure	95 psia
Characteristic Velocity (C*)	5250 ft/sec
Specific Impulse	282 sec
Minimum Impulse Bit	0.15 lb-sec
Thrust Coefficient	1.74
Nozzle Throat Area	0.133 in^2
Nozzle Exit Area	5.33 in^2
Expansion Ratio	40:1
Characteristic Length (L*)	10 to 12 in
Chamber Diameter	0.8 in
Injector - Single impinging doublet fuel cooled	
Chamber - Radiation cooled	
Propellant Valves - Poppet, coaxial flow, solenoid actuated	
Valve Opening Response	6.5 ms
Valve Closing Response	4.0 ms
Valve Synchronization	±0.25 ms

SOLID ROCKET SYSTEM TECHNOLOGY

LIST OF ACTIVE CONTRACT PROJECTS AND IN-HOUSE LABORATORY PROGRAMS

SOLID ROCKET DIVISION (RPM)

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IN-HOUSE LABORATORY PROGRAMS

(U) Investigation and Feasibility Demonstration of a Variable-Area Throat Nozzle System/Arde-Portland Inc, Paramus, N. J. / R. Edwards/AF04(611)-10749/Capt D. Stump (RPMCH)

(U) This program consists of selecting a nozzle concept for a throttlable, restartable solid rocket motor and developing and demonstrating this concept through test firings.

(U) Development Nozzle No. 4 was fired on a Char motor at the Air Force Rocket Propulsion Laboratory on July 13, 17 and 18, 1967. The nozzle test consisted of three 10-second pulses with ambient cool-down between pulses at 700 psi chamber pressure.

(U) The nozzle was found to be in excellent condition after the three firing pulses. The pyrolytic graphite pintle throat pack and the tungsten nose cap showed no degradation as a result of the 30 seconds of testing. A detailed postfire examination report (AFRPL-TR-67-313) of Development Nozzle No. 4 is being published.

(U) The final demonstration nozzle is being fabricated and is scheduled for testing in early March 1968. This test will demonstrate the survivability of the nozzle design for 120 seconds of firing time with test pulses of 800 psi to 1000 psi and 10 to 30 seconds duration.

(U) Development of Propellants Containing High-Energy Oxidizers/ United Technology Center, Sunnyvale, Calif/E. J. Walden/ AF04(611)-10786/R. D. Pallett (RPMCP)

(U) Initially the objective of this contract was the production and evaluation of a prototype propellant using nitronium perchlorate (NP) as the oxidizer; however, the emphasis of the effort was later placed on the definition of the utility of hydroxylamine perchlorate (HAP) and hydrazine diperchlorate (HP-2) when it become apparent that the feasibility of NP was severely limited due to its unstable nature.

(C) Since redirection of the contract, effort has been expended mainly in the area of compatibility studies. UTC has come to the conclusion that both HAP and HP-2 exhibit best compatibility with nonpolar compounds. While the use of unsaturated ingredients in HAP propellants does not appear to be a problem on a short-term basis, it found that the use of HP-2 in propellants demands the use of saturated ingredients.

(C) On the basis of the above information, UTC was able to successfully effect a cure with both HAP and HP-2 in the same binder system (UTREZDIOL/castor oil/DDI/MRPX). It was found, however, that the use of secondary hydroxyl UTREZDIOL will increase the pot life of HAP propellants approximately 1 hour in comparison with primary hydroxyl UTREZDIOL. The secondary hydroxyl groups were not needed in the use of HP-2 propellants.

(C) Both HAP and HP-2 formulations have been cast into micromotors and these motors have been fired successfully. The majority of motors fired showed slight progressivity; however, this is not believed to be an intrinsic property of the propellants since an AP formulation used as a standard also showed slight progressivity. A .3-lb micromotor containing a solids loading of 80% (65% coarse HAP, 15% Al) yielded a burn rate of .40 in/sec at 1000 psia with an n value of .058. An HP-2 formulation with

a solids loading of 74% (67% 100-200 μ HP-2, 7% Al) burned at a rate of 1.18 in/sec at 1000 psia with an n value of 0.36.

(C) In the area of aging, it was found that the life of an HP-2 propellant at 110°F was not more than 2 weeks. The HAP propellant, however, has shown good aging characteristics at 110°F since the beginning of the test 2½ months ago. At 135°F the HAP formulation darkened after only 2 weeks.

(U) Technical work on this contract has been completed and current effort is being expended on the preparation of the final report.

(U) Feasibility Demonstration of a Single-Chamber Controllable Solid Rocket Motor/Aerojet-General Corp, Sacramento, Calif. /C. T. Levinsky/AF 04(611)-10820/R. E. Smith (RPMMA)

(U) The objective of this program was to design, develop, and demonstrate a single-chamber controllable solid rocket motor. The technology generated provided the capability to control, on command, the thrust of a solid propellant rocket motor.

(C) During the month of July 1967, three lightweight motors were tested at Arnold Engineering Development Center (AEDC). The first motor was fired a total of six times, and demonstrated a thrust variation capability of approximately 6:1. Each pulse was extinguished and the motor permitted to cool for a minimum of 3 hours between firings. The second motor was fired a total of six times and demonstrated a thrust variation of 6100 to 4000 pounds. This motor was also permitted to cool between pulses. The third motor was fired a total of five times. The first pulse was manually controlled from the throttle on the control console. The second and third pulses were fired remotely, 2 minutes apart, and the final two pulses were permitted to cool between firings. This motor demonstrated thrust variation from 6300 to 3500 pounds. Firing pulse duration varied from 0.8 seconds on the second pulse of the first motor to 15.3 seconds on the first pulse of the third motor. The vacuum specific impulse based on AEDC-measured expended mass was 260.99, 260.98, and 262.12 lb_f-sec/lb_m for motors one, two, and three, respectively. This test series was the completion of the technical effort. Any further information can be found in the final report, AFRPL-TR-67-300 published in January of 1968.

(U) Subsonic Combustion Ducted Solid Rocket Technology Demonstration/ E. R. Flemig/Thiokol Chemical Corporation, Huntsville Division, and Ling-Temco-Vought, Dallas/AF 04(611)-10924/T.A. O'Grady (RPMMM)

(U) The objective of this program is to design, fabricate, and demonstrate a high-performance ducted rocket using a fuel-rich solid propellant sustainer motor. Design constraints representative of advanced air-launched missile system requirements have been imposed.

(C) During this reporting period, detailed analysis of full-scale direct-connect test data was completed. An average combustion efficiency of 89 percent was obtained across the range of Mach numbers from 2.4 to 3.2 at simulated altitudes from 500 to 8000 feet. A design-point specific impulse of 1704 seconds was measured corresponding to a flight-delivered impulse of 1580 seconds after correction for vitiation effect and inlet losses.

(C) Subscale inlet testing was completed, resulting in low delivered performance. The principal reason for low performance was identified as severe flow distortion resulting from separation in the subsonic portion of the inlet. Among other losses, excessive subsonic flow spillage was experienced. It was determined that the inlet design required additional development to be acceptable for free-jet testing. This forced postponement of the free-jet test program scheduled for January 1968.

(C) With the postponement of free-jet testing, the program was redirected to provide direct-connect test data at simulated high-altitude conditions. The range of conditions to be investigated will extend from Mach numbers of 2.0 to 4.0 to altitudes of 75,000 feet. The hardware will be of nominal 7-inch size as in past subscale testing. Primary motor characterization at very low mass flows is currently in progress.

(U) Prior work is summarized in:

"Ducted Rocket Technology Demonstration Program," May 1966, AFRPL-TR-66-117, AD numbers: Pt 1, Phase 1-374615 (S); Pt 2-373737 (C); Pt 3-373738 (C); Pt 4-374616 (S); Pt 5-375018 (S); Pt 6-373739 (C).

"Ducted Rocket Technology Demonstration Program," April 1967, AFRPL-TR-67-179, AD 382467 (C). The work outlined in this report is detailed in AFRPL-TR-67-322.

(U) Evaluation of Characteristics Affecting Attainment of Optimum Properties of Ablative Nozzle Components/Aerojet-General Corporation/J. Warga/AF 04(611)-10933/W.F. Payne (RPMCH)

(U) The objective of this program is to define material and process criteria that have a significant effect on the performance of ablative nozzle components. Laboratory characterization work was reported in three previous quarterly reports as listed below:

AFRPL-TR-66-3 January 1966, AD 476302.
AFRPL-TR-66-74 April 1966, AD 480407.
AFRPL-TR-66-157 July 1966, AD 486779.

(U) During this period, two identical ablative nozzles were fabricated for evaluation under AFRPL Project NOMAD using surplus Second-Stage Minuteman motors with a modified test closure compatible with single submerged nozzle. The throat and exit cone portions consist of 120° segments in order to evaluate the effects of resin content, wrap angle, resin advancement and molding pressure in a common environment. Thermocouple plugs were installed to monitor temperature at various depths in each ablative segment.

(U) The nozzles were successfully fired in August and September 1967. Posttest measurements consisted of: (1) erosion and char measurements at 33 stations and 9 positions around the circumference at each station; and (2) property measurements on char samples. Complete measurements of thermophysical and mechanical properties of virgin material and laboratory chars from trim samples were also generated for use in a computer ablation model analysis.

(U) The final report describing these results will be distributed in February as AFRPL-TR-68-29.

(U) Demonstration of a Flight-weight Cooled Nozzle/Aerojet-General Corp., Sacramento/W.H. Baker/AF 04(611)-10934/W.F. Payne (RPMCH)

(U) The objective of this program is to demonstrate a self-contained cooled throat nozzle design capable of 60-second operation in an erosive high-flame-temperature solid propellant exhaust gas environment. The throat is 2.715 inches in diameter and constructed of tantalum T-222 alloy with lithium as the cooling agent.

(U) The early portion of the program has been reported in three quarterly reports - AFRPL-TR-66-16, AD 476881; AFRPL-TR-66-91, AD 481829; and AFRPL-TR-66-172, AD 486640. This work included property measurements with the T-222 tantalum alloy, thermal analysis and elastic-plastic stress analysis including thermal stress. The nozzle design generated was fabricated and tested in July 1967 and suffered a burnthrough failure after 28 seconds. The difficulty was due to plugging of the external auxiliary coolant source employed in the demonstration test. (This external supply was used only to avoid fabricating an integral lithium reservoir in the liner, because of cost. The flight-weight version easily carries all the required coolant in an internal reservoir in the nozzle throat structure, even for a submerged configuration.)

(U) The program is now essentially repeating the earlier tests with modifications to insure adequate coolant for the ground test. The liner will be a flight-type design with internal reservoir and exit-cone self-pressurization features. The coolant vapor will, however, be simply discharged to atmosphere without the plumbing required in a flight-weight configuration. A cross section of the test nozzle is shown in Figure 1. A redundant emerging pressure supply will be incorporated to avoid the possibility of test failure from alumina plugging of the pressurization ports in the exit cone. A redundant external coolant supply will flow lithium into the nozzle through the overboard dump ports to insure that

the internal lithium level does not drop sufficiently to prevent coolant contact with the liner in the critical throat region. If the internal reservoir operates properly, the externally supplied coolant will be rejected overboard. The internal lithium supply is, of course, solid for storage purposes and must melt during the initial firing period.

(U) The test nozzle is presently in fabrication and the predicted firing date is June 1968. This firing will complete the program.

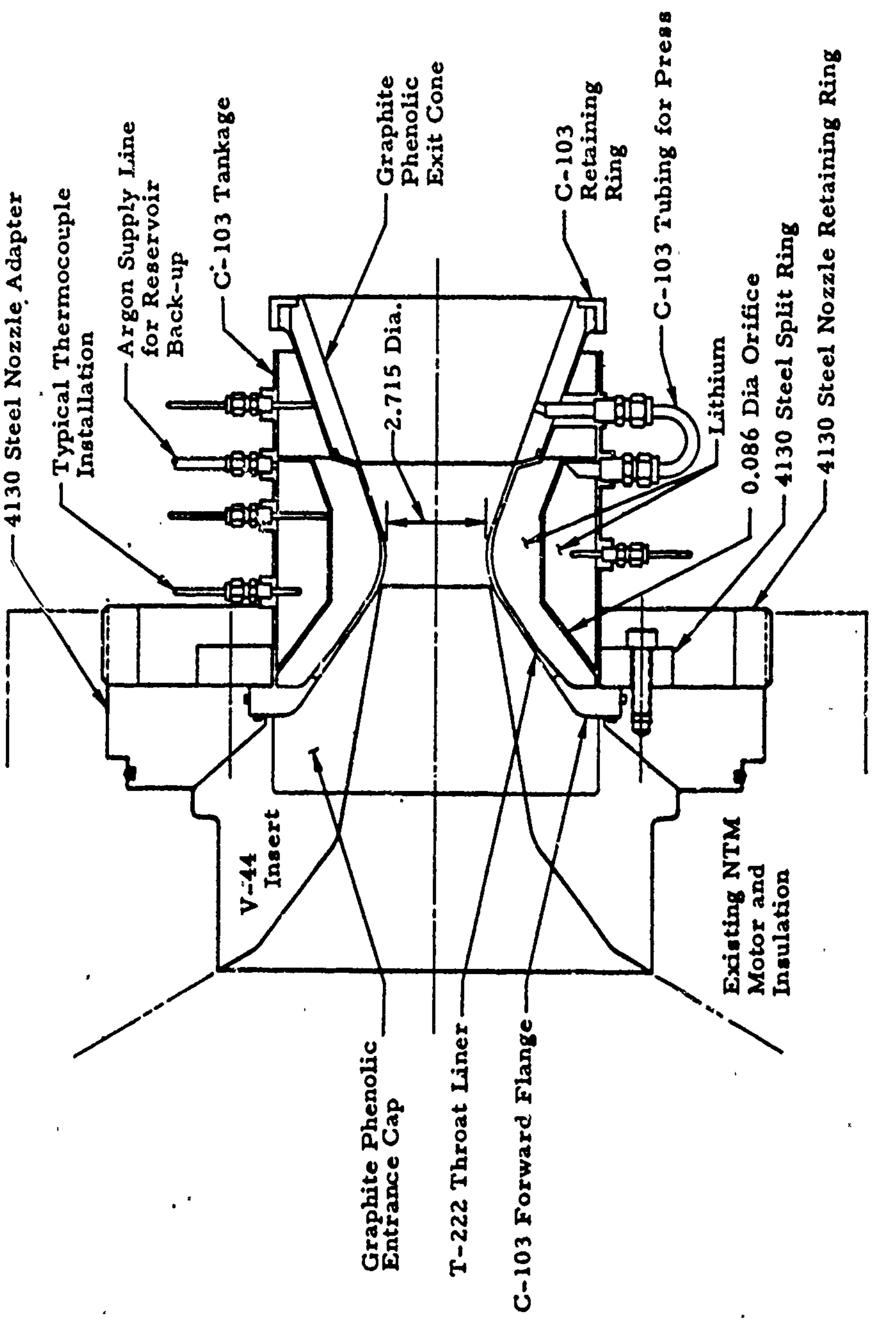

Figure 1. Design

(U) Development and Demonstration of a Chamber-Bleed Hot-Gas Thrust-Vector-Control System for Large Solid Rocket Motors/ Thiokol Chemical Corporation (Wasatch)/D. Hume/AF 04(611)-11408/Capt D. Stump (RPMCH)

(U) The 120-inch-diameter Demonstration Test Motor, static-tested on 30 August 1967, was designed as a subscale demonstration motor to test full-sized hot-gas valves designed for a 156-inch-diameter motor. The valve is sized to require four valves per quadrant on a 156-inch motor. This motor generated approximately one-fourth the mass flow of the 156-inch motor and therefore required only one valve per quadrant for TVC demonstration.

(C) The 120-inch motor was tested in the vertical (nozzle up) position. Normal ignition and operation were achieved for the first 35 seconds of the planned 120-second duration test. During this time interval, all four submerged hot-gas valves actuated as programmed, providing valve performance data. Valve responses to input signals were excellent, valve actuation loads were less than 5,000 lb, and single-valve force ratios ranging from 0.796 to 0.0845 ($4^{\circ}33'$ to $4^{\circ}50'$ TVC angles) were demonstrated at full valve flow.

(U) At 35.74 seconds the injection port insert and injection port backup were ejected from valve No. 3. The increased gas flow through the enlarged No. 3 port and direct heating of the unprotected steel nozzle shell resulted in the subsequent loss of the injection ports of valves No. 2, 3, and 4, the ejection of valves No. 2, 3, and 4, the loss of nozzle exit cone, and motor case burnthrough.

(U) The evaluation of the data obtained from the test and the hardware demonstration indicates the following:

1. The valve pintle assembly is structurally adequate and met all of its design objectives.

2. The side forces produced were slightly in excess of those required by the incentive plan.

3. Valve actuation forces were lower than anticipated, indicating superior pressure balancing characteristics.

4. The valve injection port design is inadequate.

5. The submerged nozzle performance was satisfactory considering the excessively severe flow conditions resulting from injection port malfunction.

6. All available data indicate that large submerged valves can be employed to provide thrust vector control on large solid propellant rocket motors.

(U) Based upon the failure of the demonstration test, a detailed failure analysis will be conducted to provide the necessary data for the redesign of the 156-inch hot-gas thrust-vector-control system. A design study will also be accomplished to compare the hot-gas thrust-vector-control system design for the 156-inch-diameter motor with the flexible-seal thrust-vector-control system and the liquid-injection thrust-vector-control system.

(U) Development of Castable Carbonaceous Materials for Solid Rocket Nozzles/Thiokol Chemical Corporation (Wasatch Div)/E. Benian/ AF 04(611)-11417/R. J. Schoner (RPMCH)

(U) The high costs associated with the fabrication of large solid rocket nozzles have resulted in several efforts to reduce these costs through less expensive raw materials and simpler fabrication techniques. One of the most promising of these new concepts is a carbonaceous material which is capable of being cast to the desired shape. The objective of this program with Thiokol is to develop this material for application to large nozzles and demonstrate its performance capability in several subscale tests of nozzles with 4-inch and 7-inch throat diameters.

(U) The material formulation and first four subscale nozzle test results were discussed in the last two preceding reports. Because of the failure of Nozzle 4, which used a low-pressure cure material for the throat, it was decided to attempt to reproduce the success achieved by Nozzle 3. Consequently, the fifth subscale nozzle was identical to No. 3 and was test fired on the AFRPL Char motor during December 1967. Expected test duration was 30 seconds but a burnthrough occurred near the region of the throat at approximately 20 seconds into the test. Postfire inspection of the nozzle revealed that catastrophic failure occurred in the entrance and forward exit-cone regions. The aft exit cone experienced severe gouging. Thiokol has not completed the failure analysis but the primary mode of failure appeared to be structural, resulting in spallation and excessive regression.

(U) Under IR&D sponsorship, Thiokol fabricated an 8.5-inch-throat-diameter nozzle. This nozzle was test fired by the AFRPL on a Second-Stage Minuteman Motor with a modified single-nozzle aft closure. Preliminary posttest data showed high regression in the throat but satisfactory performance for the other parts.

(U) The present contract has sufficient funds for the fabrication of a 7-inch nozzle which will be tested on the AFRPL 84-inch Char Motor. This nozzle will be fabricated to conclude the contractual effort.

(U) Evaluation of Solid Propellants Suitable for Extended Environments/ Rocketdyne, McGregor, Texas/C. Bryant/AF 04(611)-11418/ B.R. Warren (RPMCP)

(C) The objective of this program is to develop and demonstrate solid rocket propellants, liners and grain designs which will provide maximum temperature capability without degradation of motor performance. The temperature goals of the program are -75°F to 350°F.

(U) The program is separated into three distinct phases. Phase I, a laboratory investigation consisting of the evaluation of many propellant formulations, was completed by the selection of three formulations for further tailoring and evaluation. Phase II, grain design and structural analysis, is complete, with the motor drawings and grain design drawings now released.

(C) Effort on the Motor Demonstration Phase (Phase III) was resumed in November after a work stoppage of 4 months. This phase consists of subjecting the motors to vibration and extreme-temperature cycles to determine if the propellant can withstand the temperature limits of -75°F to +350°F. The motors are fired after testing with the exception of Motor 1, which is inert, and Motor 4 which will be cycled to failure.

(U) Motor 1 was used to evaluate the instrumentation of the facility and its capability to reach the temperature limits imposed by the test plan within the required time limits. These tests were successful.

(C) The extensive checkout of the inert motor (No. 1) made it possible to move through the testing sequence for Motor 2 without test problems or equipment malfunctions. This testing sequence included vibration and cycling between the temperature extremes of -60 and +300°F. All of the above cycles were performed successfully and were followed by the successful firing of Motor 2.

(C) The test plan for Motor 3 was the same as that for Motor 2 except for the final test cycle in which the temperature extremes were -65 and +350°F. The motor was then conditioned to -75°F, taken to the test stand and fired after an equilibrium skin temperature of +350°F was obtained. The entire test sequence was performed successfully.

(U) Motors 4 and 5 are to be cast in January 1968 and tested during February and March.

(U) Supply of High-Energy Solid Propellant Fuel/Dow Chemical Company, Freeport, Texas/J.H. Doerr/AF 04(611)-11461/Lt A.E. Karabela (RPMCP)

(C) The purpose of this program is to supply the Air Force with approximately 1120 pounds of aluminum hydride (AlH_3). The Dow Chemical Corporation has indicated a desire to cease operation of their Freeport, Texas, pilot plant, which is the only AlH_3 production facility. This is a result of modifications to the plant that have made continued safe operations difficult. With the completion of this contract the plant will be torn down. To date, approximately 700 pounds of magnesium-doped, diphenylamine-treated AlH_3 have been produced and shipped to users. Bulk densities as high as 0.890 g/cc have been achieved. Average thermal stabilities of 30 days to reach 1% decomposition at 60°C (determined on a modified Taliani apparatus) have been reported. This material is to be used for a number of planned propellant research and developmental efforts.

(U) Exhaust Plume Reflectivity Studies/AeroChem Research Laboratories, Inc., Princeton, N.J./H.S. Pergament/AF 04(611)-11541/ Lt R.P. Donaldson (RPMCP)

(U) The objective of this program is the theoretical development and experimental verification of a general technique for the prediction of radar reflectivity of rocket exhaust plumes. The technique will include the effects of: propellant composition, altitude up to 200,000 ft., vehicle velocity, turbulence, mixing, viewing angle, microwave frequency, and nonequilibrium reaction kinetics.

(U) The approach for this, the continuation of the original contract, consists of three phases. PHASE I, Theoretical Predictions, involves the theoretical development of gas dynamic-chemical kinetic analyses and electromagnetic wave - turbulent plasma interactions. PHASE II, Experimental Verification, involves microwave attenuation tests at Thiokol (RMD) and at AEDC, and radar reflectivity tests at RATSCAT. PHASE III, Final Determination, involves comparison of theory and experiment, improvement of the model, and predictions for Air Force missions.

(U) The technical highlights of the last two quarters of 1967 are as follows:

PHASE I. Theoretical Predictions.

(U) Progress is being made toward the development of a two-dimensional mixing and afterburning computer program. The effects of axial pressure gradients have been examined with the axisymmetric frozen mixing program. Programming of the Mixing with Equilibrium Chemistry Program is nearly completed. Two computer programs— Method of Characteristics and Nonequilibrium Streamline—have been received by AFRPL. Test cases have been run. A semianalytic expression for the special case of scattering from an overdense cylindrical plasma at

normal incidence using an exponential correlation function has been developed. The analysis of the interaction of a nonuniform radar beam normally incident on a nonuniform plasma has been completed.

PHASE II - Experimental Verification.

(U) Microwave attenuation tests at Thiokol (RMD) have been performed on liquid and solid rocket motors. Radar reflectivity measurements are presently scheduled for mid-February at RATSCAT. The effect of viewing angle and frequency will be determined for both liquid and solid rocket exhausts. Frequencies of 5000, 1250, and 150 MHz will be used. Tests at AEDC are now scheduled for January 1969. These tests will investigate the effects of missile shape, altitude and air velocity on attenuation. AFRPL will attempt to obtain actual flight-test data on a tactical Air Force missile, in order to further augment the prediction technique.

PHASE III - Final Determination.

(U) Little progress has been made in this phase, awaiting outcome of Phase II testing.

(U) One report of significance has been published during this report period:

H.S. Pergament, V.J. Siminski; "Radar Reflectivity of Turbulent Rocket Exhaust Plumes (U)", AeroChem TP-159, July 1967, Special Report.

(U) 156-Inch-Diameter Motor - One Million Pounds Thrust (Segmented Fiberglass Case) (Program 623A)/Thiokol Chemical Corp., Wasatch Div./C. Kennedy/AF 04(611)-11603/Capt R. B. Neely (RPMMA)

(U) The objective of this program is to demonstrate in a static firing the feasibility of a 156-inch-diameter solid motor utilizing a segmented fiberglass case. In addition, a large ablative nozzle, fabricated without the use of hydroclave facilities, will be tested on the motor. The case and nozzle were developed and fabricated under Contracts AF 33(657)-11301 and -11303 initiated by the Air Force Materials Laboratory, Wright-Patterson AFB, Ohio.

(U) The segmented glass case with joint seals was successfully hydrotested to 880 psig for 120 seconds, insulated and cast with propellant. During this reporting period approximately 24,000 lbs of propellant were removed from the forward segment in order to remove all detrimental voids. Modified Minuteman trimming machines and limited hand trimming were used to remove the propellant. The motor has been recast and cured successfully. This effort is a significant accomplishment in the art of propellant removal and motor repair techniques.

(U) The motor segments and nozzle will be moved to the test area and assembled for the static test in February 1968. Following the static test the segmented glass case is scheduled to be subjected to a hydroburst test.

REFERENCES

AFRPL-TR-66-22, Quarterly Technical Report No. 1, Contract AF 04(611)-11603, 7 October 1966, AD 376586.

AFRPL-TR-66-316, Quarterly Technical Report No. 2, Contract AF 04(611)-11603, December 1966, AD 803696.

(U) A Study of the Effects of Dewetting on the Physical and Ballistic Properties of Solid Propellants/E. Sutton/Thiokol Chemical Corp., Elkton Division/AF 04(611)-11605/D. Saylak (RPMCB)

(U) The objective of this program is to demonstrate the advantages of selectively dewetting the surface of a solid propellant grain from a structural and ballistic point of view. The treatment calls for the immersion of propellant in liquid Freon-12 at room temperature, i.e., under its own vapor pressure. During the treatment, the Freon will penetrate the propellant surface at a rate which varies with the binder system. When the desired depth of penetration is achieved, the Freon is allowed to evaporate off. The rapid cooling and swelling at the surface causes a partial breakdown of the oxidizer-binder bond which lowers the modulus of the treated material and, in turn, increases the strain capability. Since the density of the dewetted material is changed during the treatment, the optimum represents a tradeoff between achieving the maximum strain capability at a minimum depth of penetration.

(U) Originally, the program effort was divided into two phase: Phase I, Laboratory Testing, was designed to establish those parameters necessary to dewet the surface of the propellants under study to a depth of 1/16 inch and measure the effects on physical properties, burning rate and ignition. This phase has been completed. Phase II, Scale-Up Demonstration, evaluated the improved crack resistance and low-temperature firing capability of treated motors as a result of the dewetting technique. Two sets of ten 5-inch motors, 20 inches long, were filled with the same polyurethane and CTPB propellants used in Phase I. These motors had a CP grain configuration with a web fraction of 82%. Half of the motors from each set were treated in accordance with the procedures established in Phase I. One treated and one untreated motor from each set were set aside as controls and the rest were thermal-cycled.

(U) All untreated CTPB motors cracked at -100°F and all untreated polyurethane motors cracked at -10°F. No treated motors cracked in either set. All of the treated motors were static-fired at test temperatures of +135°F, 62°F, and -51°F for the CTPB and 135°F, 62°F, and +1°F for the polyurethane. The different low temperatures for each propellant were selected on the basis of their low-temperature ignition thresholds as determined in the ignition studies of Phase I. All motors fired successfully after having been exposed to environments beyond the capability of their untreated counterparts.

(U) The results continue to substantiate the improved structural and ballistic reliability to be gained through the Freon-12 stress technique.

(U) This contract has been ammended to include two additional phases. Phase III will attempt to achieve a more complete understanding of the oxidizer binder interaction during and after treatment. This will be accomplished using time-lapse macrocinematography techniques. Results to date have shown that a marked difference exists in the effects produced by the Freon-12 exposure to a cast and a machined surface. The visual record of the treatment shows that the most critical phase of the process is evaporation, the rate of which must be controlled to prevent thermal shock of the grain. Attempts to obtain highly magnified photos of the oxidizer binder interaction were unsuccessful due to the inability to keep the specimen, whose dimensions are changing during the swelling and evaporation phases, in focus at the desired level of magnification.

(U) Phase IV was added to the contract and provided Thiokol the opportunity to study the structural capability of stress-relieved propellant under a combined vibration-thermal cooldown environment. Due to a vibration facility limitation at Thiokol, this work resulted in an integrated effort between Thiokol and Rocketdyne. Rocketdyne will conduct a series of tests on both a treated and an untreated motor and assess to what extent the environmental capability of their propellant has been improved.

(U) The details of the Rocketdyne effort will be discussed under the report for Contract No. F04611-68-C-0017.

(U) Phases I, II and III have been completed; Phase IV should be completed in January 1968.

(U) Composite Carbide Nozzles for Solid Rocket Motors/Aerojet-General Corporation/M. Swope/AF 04(611)-11608/Capt E.M. Schneider (RPMCH)

(U) The contract AF 04(611)-11608 objective is to develop refractory composite carbide nozzle inserts for use with a 6800°F flame temperature solid propellant.

(U) The two-phase program will consist of material fabrication optimization and nozzle design, fabrication and test firing. Specific goals are to: (1) develop two experimental composite bodies, a microcomposite and a high-density carbide liner backed with a hypereutectic substrate, and establish the best fabrication technique for obtaining the desired sintering characteristics, phase relationships, and crystallographic structures; (2) determine ambient and elevated-temperature mechanical and physical properties related to thermal shock resistance; (3) verify the thermal shock resistance and the oxidation resistance of the selected candidate composites; and (4) demonstrate the composite capabilities when utilized as a rocket nozzle insert tested with a 6800°F aluminized solid propellant at chamber pressure of 700 psi nominal for 60 seconds duration.

(U) During this reporting period, work has continued with the physical and mechanical property testing of the tantalum-hafnium-carbon microcomposite alloy, the tantalum carbide hypereutectic fabrication procedures have been established, microcomposite thermal shock and chemical corrosion testing has been accomplished and full-scale demonstration nozzle design drawings have been submitted.

(U) The microcomposite property data is presented in AFRPL-TR-67-207 dated July 1967, AD 817208. The processing parameters of the hypereutectic include blending the desired powders of tantalum carbide and carbon to an exact composition, hot-pressing to densify the compact, inserting the compact into a graphite fusion casting mold, and resistance-heating to 3450°C and drop-casting the hypereutectic compact into a

preshaped mold. The furnace operates under a 60-psi helium atmosphere which permits close compositional control. Graphite die design is very critical due to the necessity for a uniform hypereutectic melt zone. Hypereutectic specimens $1\frac{1}{2}$ inches in diameter and 3 inches long are being cast to form specimens for materials property characterization studies. Hyper-environmental simulator tests have been conducted at cold-wall heat fluxes of 2800 to 3000 BTU's per ft^2 second and 400-psi nitrogen pressure on microcomposite specimens with 3/8-inch throat diameters. Specimens did not fail when exposed up to 60 seconds test duration. Three out of four specimens exhibited hairline radial cracks although none of the specimens came apart. When exposed to simulated solid propellant rocket exhausts, the microcomposite exhibited erosion rates less than 1 mil per second for a 60-second test at 400 psi.

(U) Remaining effort includes scaleup of the microcomposite and hypereutectic alloys to provide $2\frac{1}{2}$-inch-inside-diameter nozzle inserts, hypereutectic materials property characterization, nozzle demonstration testing, and posttest evaluation. Another Interim Report will be published in February 1968. The program is scheduled for completion in June 1968.

(U) A Study of Heat-Transfer Characteristics of Hot-Gas Igniters/ Rocketdyne/J. Wrubel/AF 04(611)-11613/Capt C.E. Payne (RPMCP)

(U) The goals of this contract were the determination of the characteristics of the heat transfer from pyrogen-type igniter systems to solid propellant motor grains. The previous years effort (Contract AF 04(611)-9884) entailed the study of center-perforated solid motor geometries including both cylindrical perforations and cylindrical perforations with slots. The current effort entailed the study of star- and cylindrical-perforated conecyl grains. Both the solid propellant grain and the igniter gas flow were simulated, the grain by a calorimetric metal tube and the igniter flow by heated nitrogen. Although appropriate heat-transfer relationships were determined for all geometries, the relationships were graphical in nature; unfortunately it was not possible to eliminate or normalize all geometry factors. That is, in order to utilize the relationships, assumptions concerning igniter geometry would necessarily be made. Additionally, it was not possible to predict the jet impingement point of the igniter stream. This is an important variable due to the fact that it represents the zone of maximum heat transfer and consequently the point of first ignition. Since flame-spread rates in the upstream and downstream directions are not equal, the prediction of total ignition delay is dependent upon knowledge of the point of first ignition. For most cases the impingement point was found to occur two motor diameters downstream from the igniter nozzle. The results from this program are serving as an input for the Igniter Design Handbook with CETEC Corporation, Contract F04611-67-C-0083.

(U) The Final Report for this contract was distributed in July 1967. The report number is AFRPL-TR-67-267, AD 821548.

(U) Combustion Instability Studies of Extinguishable Propellants/ Hercules, Allegany Ballistics Laboratory/Dr. R. Miller/ AF 04(611)-11619/Capt C.E. Payne (RPMCP)

(U) The objectives of this program are to determine the relationships between solid propellant combustion instability and extinguishability, to formulate improved extinguishable propellant selection criteria, and provide basic information in the fields of solid propellant combustion instability and extinguishment.

(U) The experimental portion of this program has been completed. All that remains is the approval and distribution of the final report.

(U) The investigations that were made on the program involved the testing of five propellants, both composite and double base. The formulations included easily extinguishable propellants and those which were difficult to extinguish. Nonacoustic instability properties were measured in an L* burner. Acoustic instability phenomena were examined in a T burner. The combustion characteristics of all propellants were monitored in a combustion bomb with high-speed photography.

(U) The program results indicate that there is a different mechanism of extinguishment for double-base propellants as compared to composite propellants. The development of a concise analytical model was not possible. However, the indicated mechanisms for the two types of propellants point to a kinetic limited case for composites and a physical removal of the flame zone for double-base propellants. The burner and motor test data were confirmed via laboratory tests during which a mass spectrometer was utilized.

(U) In the demonstration phase of the program, a composite and a double-base propellant were formulated. These propellants were formulated to have good extinguishment properties based on the results of the prior

portion of the program. The double-base propellant demonstrated satisfactory extinguishment properties. The composite propellant did not extinguish. The lack of success with the composite propellant was attributed to an approach of the burn-rate slope of this particular propellant to a zero level at the low end of the pressure curve. This phenomenon has been observed to occur with other composite propellants and justifies the measurement of burn-rate data to low-pressure regions.

(U) Study and Demonstration of Paper Phenolic Components/Thiokol Chemical Corporation (Elkton Division)/J. Edwards/AF 04(611)-11621/W. F. Payne (RPMCH)

(U) The objective of this program was to determine the potential of paper phenolic laminates as a cost-effective structural material. Properties of paper phenolic materials were investigated and several applications were evaluated, including an M58A2 Falcon motor case, the 2.75 FFAR rocket, Tomahawk igniter, the 1.0-KS-25 spin motor and XM156 parachute flare. The studies concluded that paper phenolic was not an attractive structural material for performance-sensitive applications, primarily due to the low strength in the longitudinal direction of commercially available material. The studies have been completed and are reported in AFRPL-TR-67-320.

(U) Advanced Upper-Stage Chamber-Bleed Secondary-Injection Thrust Vector Control/Thiokol Chemical Corporation, Wasatch/C. Lancaster/ AF 04(611)-11627/Capt D. Stump (RPMCH)

(U) The objective of this program was to design, develop and demonstrate a flight-weight Hot-Gas Secondary-Injection Thrust-Vector-Control System for advanced upper-stage ICBM solid rocket motors.

(U) The Demonstration Motor was successfully static-tested on 12 July 1967. The motor ignited and operated normally. The hot-gas valves operated as programmed for the duration of the test. All motor and valve hardware was in good condition after the test. The motor chamber pressure reached a maximum of 784 psi at 6.4 seconds and averaged 724 psi over a web time of 56 seconds. The maximum axial thrust was 24,900 lb_f and averaged 23,200 lb_f over the 56-second web time.

(C) A maximum single-valve vector angle of 2.45° was recorded at 11 seconds when Valve 1 was full open. At 26.9 seconds, with Valves 2 and 3 full open, a biaxial vector angle of 2.8° was recorded.

(U) The valve design demonstrated is adequate to withstand all environments to which it has been exposed which range from 5700°F to 6500°F (20% Al), pressure up to 780 psi, and durations up to 58 seconds. Based on observed valve condition and design considerations, the valve design is capable of withstanding these conditions for durations up to 80 seconds with no design modifications.

(U) A TVC systems comparison will be conducted for a Third-Stage Minuteman-type nozzle comparing HGSITVC, LITVC, and flexible-bearing TVC Systems. Each system will be independently optimized to the same applicable mission requirements, using fixed Wing VI Stages I and II. The results of this study will appear in a separate volume to the final report published under Contract AF 04(611)-11408.

(U) The program has been completed and the final report published - AFRPL-TR-67-262, November 1967.

(U) Evaluation of Low Cost Materials and Manufacturing Processes for Large Solid Rocket Nozzles/Aerojet-General Corporation, Sacramento/J. Warga/AF 04(611)-11646/W. F. Payne (RPMCH)

(U) This program investigated the performance and cost effectiveness of using commercially available low-cost ablative materials as liners for large solid rocket nozzles. Eleven firings were conducted employing a single submerged-nozzle configuration with surplus second-stage Minuteman motors with a modified aft closure. The test reports issued for the tests during this reporting period are listed below:

AFRPL-TR-67-171	July 1967, AD 817713
AFRPL-TR-67-172	August 1967, AD 819390
AFRPL-TR-67-173	September 1967, AD 820863
AFRPL-TR-67-234	September 1967, AD 821437

A final report has been completed and distributed as AFRPL-TR-67-310 dated December 1967.

(U) The results indicate that the cost of plastic parts for a 156-inch nozzle could be reduced by up to 40%, by use of the materials evaluated in this program. This was determined by use of a cost/performance effectiveness model (explained in final report) based on a typical 156-inch nozzle design and the firing results obtained with the 8.5-inch-diameter throat nozzle on the Minuteman motor. Table I shows selected typical results for the throat approach, throat, and exit cone. Unconventional materials such as Kraft paper phenolic, cotton phenolic and asbestos performed well in throat approach (backside flame surface for a submerged configuration) and exit cone. Cheaper versions of conventional materials, such as double-thickness fabric and previously untried reinforcement fibers, were very attractive for throat inlet and throat extension applications. The Pluton B fibers in MXC-31 and the Avceram

codeposited carbon-silica fibers performed well and should receive continued development and evaluation. In the throat region, the environment is sufficiently severe so that cheaper materials do not result in improved cost effectiveness.

(U) The most cost-effective materials found for the 156-inch nozzle were Kraft paper for the throat approach, crocidolite asbestos for the exit cone and codeposited carbon-silica (AVCERAM) material for the entrance cap, throat inlet, throat and throat extension.

TABLE I

COST/PERFORMANCE EFFECTIVENESS OF ABLATIVE MATERIALS

TYPICAL RESULTS

Location	Material	Material Cost $/lb	C/PE
Throat Approach			
	FM-5272 paper phenolic	2.00	3.53
	WB-2212 BAP asbestos	3.60	2.31, 2.06
	MXA-6012 asbestos	1.85	1.74, 1.62
	*FM-5131 silica	6.00	1.00
Throat			
	4034N carbon	20.74	1.05
	*MX-4926	24.65	1.00
	ACXF-G79 graphite	20.65	0.96
	MXC-31 carbon	25.90	0.76
	*FM-5064 carbon	35.22	0.75
Exit Extension			
	FM-5525 asbestos	2.00	1.45
	KF-418 cotton phenolic	1.50	1.26
	FM-5272 paper phenolic	2.00	1.24
	MXA-6012 asbestos	1.85	1.23
	*FM-5131 silica	6.00	1.00
	MXA-198 asbestos	4.20	0.58

* Evaluated in AF 04(611)-10933

(U) Advanced Thrust-Vector-Control Preliminary-Design Computer Program/Thiokol Chemical Corp, Wasatch Div/D.E. Hume/ AF 04(611)-11647/Lt V. L. Olivier (RPMMD)

(U) The objective of this program was to develop a preliminary-design computer program for the design and performance evaluation of numerous thrust-vector-control (TVC) systems.

(U) The computer program developed provides a highly versatile and comprehensive tool for making performance tradeoffs and comparisons between many of the most commonly used TVC systems. Included in the computer program are TVC systems for both movable and fixed nozzles.

(U) Included in the movable nozzle category are the following nozzles:

1. Hinged
2. Supersonic splitline
3. Trapped ball and socket
4. Flexible seal
5. Submerged gimballed
6. External gimballed

Included in the fixed nozzle category are the following TVC systems:

1. Hot-gas injection
2. Liquid injection
3. Jet tabs
4. Aerodynamic lifting surfaces

(U) In addition to the analytical capability of the program, the computer program has preliminary design information stored within which would be useful for making quick engineering-design estimates.

(U) The present status of this program is that the technical effort is complete. The final report has been distributed.

(U) REFERENCES

1. An Empirical Performance Model of Secondary Injection for Thrust Vector Control, LMSN Huntsville Research and Engineering Center, Contract NAS 8-11077, October 1964.

2. Final Report - Design Criteria for Hot-Gas Secondary-Injection Thrust-Vector Control of Solid Propellant Rocket Motors. Vols I and II, AFRPL-TR-65-39, Contract AF 04(611)-9075. Thiokol Chemical Corporation, Brigham City, Utah; February 1965; CONFIDENTIAL. A) numbers: Vol I, Bk 1-357243; Bk 2-357246; Vol II-357247.

(U) Minuteman (Product Support Program) All-Solid PBPS Technology Program/B.A. Simmons/Aerojet-General Corporation, Sacramento/ F 04(694)-734/Lt R. S. Quintana (RPMMA)

(U) The primary objective of this program is to develop an extinguishable axial solid propellant and a low-flame-temperature gas generator solid propellant. A secondary objective is to demonstrate the performance of a variable-area nozzle motor with multiple restarts, using a hydrazine gas generator igniter.

(C) (U) Gas Generator Propellant Development.

(C) The propellant screening tests, using 1-, 10-, and 60-lb grains, on the gas generator candidate propellant formulations have been completed. The formulation is a propellant containing a polybutadiene (HTPB) binder, with ammonium perchlorate (AP) and RDX oxidizers, and ammonium sulfate as a coolant. The propellant exceeds the specific impulse goal of 195 seconds and operates at 2141°F.

(C) A double-base propellant formulation, consisting of Ball Powder B and TMETN, was also considered and was acceptable in most respects but suffered from poor ignition at low pressures (150 psia) and an unusually high π_k (1.6). Both the composite and double-base formulations produce 6% carbon.

(C) (U) Axial Motor Propellant Development.

(C) From the 15 formulations screened, a nonaluminized propellant containing NPPU binder, and RDX and AP as the oxidizer, was selected for scale-up and use in the system demonstration test. The goals of P_{dl} >5 psia, I_{sp} delivered >230, and density >0.059 were exceeded.

(C) A 5% aluminum formulation containing NPPU binder, and RDX and AP as the oxidizers was also considered. However, the propellant reignited at sea level and suffered from unstable combustion.

(C) The nonmetallized propellant will be tested in February 1968 at simulated altitude conditions at AGC with a 95-lb (HTPB binder and AP oxidizer) gas generator operating at 625 psia for 56 seconds. The 73-lb axial motor which operates at 201 psia for 13 seconds, will be pulsed four times.

(C) (U) Variable Area Nozzle Motor Tests.

(C) A pintle nozzle motor with a dual end-burning nonaluminized NPPU solid grain was tested on 25 August 1967 using a decomposed hydrazine ignition system. Of the 21 planned pulses, five were accomplished as scheduled. During a 40-second off period the pintle was reinserted into the nozzle and the grain reignited. After extinguishment the grain again reignited several times until propellant burnout. Analysis showed the autoignition temperature and critical pressure for ignition had been exceeded because of insulation outgassing, propellant pyrolysis, and heat radiation from the pintle.

(U) The second test using multiple solid igniters was cancelled because of the extensive modifications required.

REFERENCES

1. GDC-ACX-67-024, Advanced PBPS Study, Dec 1967, Secret Report, AF 04(694)-965, General Dynamics, Convair Division.
2. AST-MP-Monthly Technical Progress Reports, All Solid Technology Program, Mar 67 - Nov 67, Confidential Reports, AF 04(694)-734, CCN-75, Aerojet-General Corporation, Sacramento.

(U) Minuteman (Product Support Program) Postboost Propulsion Demonstration Program/Hercules, Inc., ABL/D. Sine/ AF 04(694)-903/Lt R.S. Quintana (RPMMA)

(U) The objective of this program is to develop an extinguishable solid axial motor propellant and to demonstrate and define the performance of a hydrazine-augmented solid propellant axial motor for PBPS application.

Axial Propellant.

(U) The axial motor propellant screening tests have been completed on six candidate propellants. These tests include the determination of P_{th} (threshold ignition pressure), physical properties, processibility and P_{dl} and L* extinguishment characteristics. At the present time, a propellant designated FMA has been selected. Its physical properties are in excess of the goal of 100 psi tensile strength and 40 to 60% elongation. The heat flux required to ignite the propellant is three times that required to ignite current available extinguishable formulations. In addition, the K_{cr}-L* relationship for extinguishment is superior to existing formulations.

System Tests.

(C) The first system demonstration test of the 5 lb/sec gas generator and a 300-lb axial motor was conducted in September 1967. The motor performed successfully for three of the planned 10 cycles. The axial thruster did not extinguish after pulse 3 and axial propellant was consumed on pulse 5. Gas generator operation was normal with ignition delays of $<$300 m.s. Axial motor chamber pressure increased over design pressure due to propellant erosion. The erosion increased the propellant burning surface area which caused the K_{cr}-L* criteria to be exceeded, not allowing permanent extinguishment.

(C) Several injectors were evaluated for the second system test which was conducted at ABL on November 17, 1967 at ambient pressure conditions. Four 1 lb/sec gas-generator units, a more refined feedback-control system and a single-sonic-orifice injector were used. The demonstration system was controlled by pressure feedback to within ±5 psi of the planned pressure level. The motor was successfully extinguished for the commanded "off" times for 7 of the 10 planned pulses and 42 of 51 seconds total "on" time and 163 seconds of the planned 205-second duty cycle. Reignition occurred after the remaining three planned pulses, and all the propellant was consumed during additional pulsing in an attempt to promote extinguishment.

(U) The third system demonstration using the improved motor propellant, FMA, was conducted at AFRPL under simulated altitude of 115,000 ft on 18 January 1968. The planned 10-pulse duty cycle was accomplished and axial propellant was recovered.

REFERENCES

1. GDC-ACX-67-024, Advanced PBPS Study, Dec 1967, Secret Report, AF 04(694)-965, General Dynamics, Convair Division.

2. NPO Conf. 0051 - Monthly Technical Progress Reports - Minuteman PSP - Post Boost Demonstration Program, Jan 67 - Nov 67, Confidential reports, AF 04(694)-903, CCN-27, Hercules, Inc., ABL.

(U) Packageable High-Expansion-Ratio Nozzles for Solid Propellant Rocket Motors/Aerojet-General Corporation, Sacramento/C. Auble/ F04611-67-C-0005/W. F. Payne (RPMCH)

(U) The objective of this program was to develop and demonstrate practical, usable, packageable exit cones which can be stored for extended periods, deployed reliably in less than 1 second and easily scaled for direct application to future high-performance solid rocket systems, including thrust vector control. The demonstration testing will be performed with surplus Skybolt motors. Two concepts have been developed: one with a convoluted thin metal exit cone and the second with an elastomeric liner supported by a pressure-stabilized cloth structure known as "Goodyear Airmat". The design details and bench tests are described in the reports listed below:

AFRPL-TR-67-233, "Packageable High-Expansion-Ratio Nozzles for Solid Propellant Rocket Motors" August 1967, AD numbers: Vol I-820623; Vol II-820625.

Volume I: Task I Deployment and Packaging
Task II Design Analysis

Volume II: (Goodyear Aerospace Corporation - Fabrication and Testing of Airmat Structures)

(U) The Demonstration Program consists of five tests in the J-5 cell at AEDC, with testing to begin in January 1968.

TEST NO.	EXIT CONE DESIGN	TVC SYSTEM
1	50/1 fixed plastic cone	Freon LITVC
2	Elastomeric - Airmat	Freon LITVC
3	Convoluted Metal	Freon LITVC
4	Elastomeric - Airmat	Gimbal actuation
5	Convoluted Metal	Gimbal actuation

(This page is Unclassified)

(U) The bench tests to demonstrate actuation of the Skybolt nozzles from folded configuration to deployed configuration in less than 1 second were completely successful.

(U) Investigation of the Air-Augmented Rocket Combustion and Mixing Process/Atlantic Research Corporation/Dr. K. Woodcock/F04611-67-C-0011/Lt H. Joonsar (RPMMM)

(U) The objective of the program is to obtain secondary chamber combustion and heterogeneous mixing data applicable to the design of air-augmented rocket systems.

(U) The first task experimental investigations include metal and metallic compound ignition and combustion in air, including gross propellant combustion reaction kinetics, and the effect of varied air-flow parameters upon secondary chamber combustion of the fuel-rich primary exhaust products. The second task is for the purpose of developing an analytical model of the secondary chamber combustion-mixing phenomenon. This developed model will be used to determine the critical combustion flow and transport parameters which effect efficient motor operation.

(U) Effort has been concentrated on design, fabrication, and checkout of the hardware components necessary for high-temperature air-propellant simulation tests. The propellant simulant will be metallized (boron, zirconium, or aluminum) slurries having chamber combustion temperatures as high as 3000°K. The air will be supplied at temperatures from ambient to approximately 1300°K (Mach 4.1, sea-level, standard day conditions). The tests will follow a logical increase in test complexity including nonreactive gases and solids, and reactive gases and reactive solids experiments.

(U) Work that has been done through the November 1967 time period in analysis has been to investigate some of the restrictions on the critical conditions of the two-dimensional-mixing analysis. The effect of velocity and thermal lags at the start of mixing has been studied and expressions derived for both. Also, results of two-phase mixing of an underexpanded

sonic jet exhausting into an ambient atmosphere are being analyzed. Calculations for the specific exhaust conditions (like velocity ratio, temperature ratio, and particle loading) are in progress.

(U) Additional effort has been expended on adjusting the particle feed system in order to control the number of boron particles passed into and through the heat-up chamber. During these tests the first attempts have been made to ignite these boron particles. Preliminary results indicate that ignition has been achieved. The test conditions are currently being refined as necessary to coordinate particle feed rate, particle residence time, and valve operation as required to pass heated particles into the ignition chamber.

(U) Work under this program is reported in "An Experimental and Analytical Study of Coaxial Jet Mixing," March 1967, AFRPL-TR-67-71, AD 809392.

(U) Supply of a High-Energy Solid Propellant Fuel/Ethyl Corporation, Baton Rouge, La./E.M. Marlett/F04611-67-C-0021/Lt A.E. Karabela (RPMCP)

(C) The overall objective of this program was to supply beryllium hydride (BeH_2) for Air Force propellant development contracts. The emphasis was placed on production of high purity, improved bulk density (better than 0.30 gm/cm^3), and reproducible beryllium hydride. In addition, a small-scale effort was devoted to a materials investigation and pyrolysis study in an effort to improve the quality and reproducibility of the BeH_2 material. Work on this program began in October 1966 and was completed in August 1967. A total of 247 pounds of beryllium hydride was produced and shipped to various users. Average purity for the entire production was 95.5% (by weight) BeH_2. The average bulk density was 0.32 gm/cm^3.

(U) Development of Fuel-Rich Propellants for Air-Augmented Rocket Applications/Thiokol Chemical Corporation (Huntsville Division/ E. R. Flemig/F04611-67-C-0035/Lt D. J. Davis (RPMMM)

(U) The objective of this program is the development of fuel-rich propellants through the determination of secondary combustion characteristics and tailoring of mechanical and ballistic properties to meet air-augmented rocket propulsion system requirements.

(C) The first phase consisted of evaluations and optimization of the mechanical, safety, and ballistic properties for candidate propellant formulations. Emphasis was given to air-augmented system performance in selection of candidate formulations. Nine propellant formulations were selected with metal loadings ranging from 40% to 65% boron, 22% to 54% aluminum and a 20% boron, 40% aluminum mixture. The selection was based on thermochemical analysis, small-scale motor firings, cost considerations and processibility criteria. Tailoring of the ballistic parameters, processing characteristics, and mechanical properties required of an air-launched missile was accomplished for each candidate propellant in phase two. Secondary combustion testing in both laboratory scale (25 to 50 gram) and large-scale 7-pound motors lead to the selection of three propellant formulations for direct-connect testing over a broad range of simulated flight conditions. The shrouded and ducted rocket propellant chosen for operation with air-to-propellant ratios of 1 to 30 was 40% boron/32% ammonium perchlorate/22% hydrocarbon binder/6% burn rate and cure catalysts. The two ducted-rocket propellant formulations chosen for operation at air-to-propellant ratios of 10 to 30 are 54% boron/22% ammonium perchlorate/17% hydrocarbon binder/7% burn rate and cure catalysts and 58% boron/20% ammonium perchlorate/15% hydrocarbon binder/7% burn rate and cure catalysts. The 40% boron propellant was chosen due to its utility as both a shrouded- and a ducted-rocket propellant. The 54% boron was chosen because of the excellent afterburning and was the highest bimodal blend of amorphous and crystalline

boron that would successfully afterburn. A bimodal blend of boron is required for better processing characteristics at the higher boron loadings. These propellants have been successfully scaled-up to 20-gallon mixes and are being tested in the direct-connect mode using 11-pound motors. Direct-connect testing will be completed in February 1968.

(U) The detailed results from the first half of the program may be found in the semiannual technical report, "Development of Fuel-Rich Propellants for Air-Augmented Rocket Applications," July 1967, SATR-782-1, AD 382875. Distribution of the final report is scheduled for April 1968.

(U) Solid Rocket Structural Integrity Information Center/University of Utah, Salt Lake City, Utah/Dr. M. L. Williams/F04611-67-C-0042/ Lt S. W. Beckwith (RPMCB)

(U) The objectives of this program are twofold: one is to provide a literature indexing and abstract service for the solid rocket community in the area of solid rocket structural integrity; and the other is to define the magnitude of the loads which solid propellant rocket motors may encounter during their lifetimes.

Solid Rocket Structural Integrity Abstracts - M. L. Williams and F. R. Wagner (editor)

(U) Two issues of the quarterly SRSIA were distributed during the past 6 months. The lead article in the July issue (Ref 1) was written by Dr. Harry Leeming of Lockheed Propulsion Company on the stress analysis-design of the Lockheed 156-inch solid motor. The article details the procedures used to compute grain safety factors under conditions of ignition (pressurization) and thermal storage. A CONFIDENTIAL volume of the SRSIA is in preparation and should be distributed during the next report period.

Load Definition Study - M. L. Williams, F. R. Wagner, and J. E. Fitzgerald

(U) Work in this area was initiated during the month of July. The present study will emphasize the shock and vibration loads which rocket motors encounter during transportation and handling since these are the least known and hence result in the most unrealistic test requirements. Considerable effort was expended to determine vibration environments for various operational modes and conditions. A literature search was initiated and data has been requested from the Polaris, Minuteman, Sparrow, and HiBEX programs. Much of this data is on limited distribution and the University has had considerable trouble obtaining access to it.

(U) REFERENCE

Leeming, H., "The Structural Design of a Large Solid Rocket Motor Grain", Solid Rocket Structural Integrity Abstracts, Vol 4 No. 3, July 1967, AD 822266.

(U) Fracture Criterion for Pressurized Vessels/University of Utah/ Dr. E. S. Folias/F04611-67-C-0043/W. F. Payne (RPMCH)

(U) The objective of this program is to develop a fracture criterion for cylindrical and spherically curved surfaces containing finite cracks by comparing linear elastic stress-field solutions with the established solutions for cracks in flat sheets. The general effect of curvature is to elevate crack stress fields; prediction of critical crack size from flat specimens inevitably results in predicted critical crack lengths larger than measured critical crack lengths in thin pressurized shells.

(U) The analytical work is progressing well and two papers have been released for publication. The first paper was, "A Cylindrical Shell Containing a Peripheral Crack," by E. S. Folias. The second paper is entitled, "On a Plate Supported by an Elastic Foundation and Containing a Finite Crack." The results show that the flat plate and curved component stresses (σ_p and σ_{shell}, respectively) can be related by a factor of the form:

$$\frac{\sigma_{shell}}{\sigma_p} \approx \frac{1 + f(c/\sqrt{Rh})}{1 + g(c/\sqrt{Rh})}$$

where the functions f and g are evaluated by integral solutions to the basic differential equations.

(U) The experimental work will consist of burst tests on spherical shells containing fatigue cracks. Spherical shells manufactured of copper, aluminum, steel, and titanium will be tested. The shells are primarily 3.75-inch-radius spheres with thicknesses over the range of 0.010 to 0.090, primarily 0.023 and 0.063 inches. A limited amount of plate material from each alloy is also available for flat specimen tests.

(This page is Unclassified)

(U) Development and Test of High-Energy Solid Propellant
Inc., (Bacchus)/R. Keller/F04611-67-C-0046/R.C. M

(C) In a previous program, the Hercules Company demon BeH_2 propellants could deliver specific impulses in exce I^{15}1000-14.7. This program is to provide tailoring techn to achieve a variety of burn rates, densities, and mechan to demonstrate a near-optimum formulation in a 40-lb furnish BATES grains of this propellant. A del is required.

(C) Propellant burn rates at 1000 psi from 0.56 in/sec to have been achieved. The lower burn-rate formulat degradation in delivered Isp down to 277 sec. Burn-ra these formulations are nominally 0.55. The highest delivered an Isp of 283 to 284 sec in a nominal 5-lb properties of these formulations have been good (e.g., and tensile strengths of 75 psi). A scale-up formulation has been selected and is designated VKG. The formulation is:

NC	Nitrocellulose	5.0%
PGA-TDI	Polyethylene glycol adepete-tolylene diisocyanate	2.0%
Be	Beryllium	3.8%
Beane	92-96% pure BeH_2	13.0%
HMX	Cyclotetramethylene tetranitramine	25.2%
2NDPA	2-nitrodiphenylamine	1.0%
NG	nitroglycerine	50%

The theoretical Isp of this system is 309 sec. The expected delivered Isp is 284 sec in a 15-lb charge. The burn rate is 0.70 in/sec at 1000 psi.

Propellant VKG has a density of 0.0502 lb/in^3. Near future work includes fabrication and testing of 15- and 40-lb motors and production of six BATES grains.

(C) This effort completes AFRPL investigations into BeH_2 double-base propellant development for the time being. The final propellant appears to be an adequate example of the potential of such systems. It is not claimed to be a fully optimum propellant but a valid example of what is obtainable. Considerable data on the tailoring of similar systems has been obtained. Safety properties, although not as good as desired, are adequate. The structural integrity of propellants of this type can be good. Only two major areas remain unexplored: these are propellant shelf life (aging characteristics) and large-scale processing characteristics (scale-up).

(U) Development of Pyrolytic Graphite Coatings for Solid Rocket Nozzles/ Atlantic Research Corporation/G. Olcutt/F04611-67-C-0047/ R. J. Schoner (RPMCH)

(U) The feasibility of using pyrolytic graphite coatings for high-temperature rocket nozzle applications has been proven under several previous efforts. However, certain areas must be further investigated before this material can be utilized for advanced solid motors. The objective of this program is to extend pyrolytic graphite (PG) coating technology to the point where it can be used, with confidence, for various mission applications.

(U) Phase I of the program is to develop fabrication techniques for manufacturing coatings capable of minimal regression at 6500°F and 800 psi for up to 100 seconds at 1-inch and 2.5-inch throat diameters. To accomplish this phase a subcontract was let to Union Carbide Corporation (UCC) to coat inserts selected by Atlantic Research Corporation (ARC). This approach was to serve the two-fold purpose of providing a production source for the inserts and allow the maximum number of substrates to be investigated under this program for minimal cost. To date, however, Union Carbide has been unsuccessful in its attempts to produce flaw-free coatings. The explanation for this is that UCC has not been able to vary the PG thickness along the substrate in the manner prescribed by ARC. This has resulted in too-thick sections at the ends of the inserts, and the associated high-discontinuity stress causes delamination. ARC has been able to obtain varying-thickness coatings in their own facility but, because of size limitations, must resort to processing the coatings one at a time.

(U) Phase II of this contract is to investigate the ability of the coated inserts to withstand the chemical attack which occurs in a rocket environment. A subcontract has been let to the Aerotherm Corporation to modify the computerized techniques they developed under AF 04(611)-9075. These modifications will provide for the capability to analyze the highly anisotropic

(This page is Unclassified)

inserts represented by PG coatings. In addition, Aerotherm will determine chemical kinetic data for the reactions of PG with H_2O, CO and CO_2. These reactions represent the main forms of chemical attack on the inserts and the data achieved will allow us to predict the coatings' response to nozzle environments. The prediction techniques will be verified by several rocket motor tests of different environments.

(U) The capability of the insert to perform in a restart environment will be investigated in Phase III. Several tests were to be conducted at Philco in the Solid Propellant Simulator for varying duty cycles.

(U) Progress has been slow to date because of the difficulties described in the second paragraph. As a result of the inability of UCC to provide adequate inserts, ARC will produce all remaining inserts. Many of the substrate materials which were used in the UCC runs will be reexamined at ARC. This redirection will reduce the scope of the Phase III, Restart Evaluation. Motor testing will be accomplished at ARC with an end-burning, uncured solid propellant motor thus limiting the evaluation to cold restarts. The Aerotherm effort will be completed during February and will be reported on in the next interim report to be published by ARC during March. More-detailed information concerning the deposition studies can be found in the first interim report published by ARC on 5 September 1967, Report Number AFRPL-TR-67-245, AD 819788.

(U) Investigation of the Thermal-Mechanical Stability of Tungste ι Alloys for Restart Applications/TRW Systems Group/J. Bohn/F046:·-67-C-0050/Capt E.M. Schneider (RPMCH)

(U) This investigation involves parallel experimental and analytical activities devoted specifically to the problems of relating materials behavior to the environmental conditions of the rocket nozzle. The objective of the investigation is to measure and predict the magnitude of permanent deformation occurring after successive solid rocket motor firings. In laboratory experiments, tungsten specimens are subjected to transient thermal environments comparable in severity to the solid rocket motor, and the temperature-time-deformation response of these specimens is measured in detail. The mechanical properties required for analysis are measured under conditions prescribed by the thermal-stress environment. The variation in microstructure as a function of time and temperature is related to these property measurements. The severity of the thermal stress environment is determined from a thermal analysis of baseline solid rocket nozzles. The baseline is represented by a nozzle with an inside throat diameter of 2.5 inches and test parameters of 700 psi motor chamber pressure, 6200°F propellant flame temperature, and 60-second test duration.

(U) A thermal-stress analysis is performed to calculate deformation in the thermal-stress specimens, and the analytical and experimental results are compared. These results form the basis for interpretation of the material behavior and the development of the most realistic analytical methods.

(U) Four tungsten-base materials are being considered: pure wrought tungsten, large-grain arc-cast tungsten, tungsten-2% thorium oxide, and tungsten-25% rhenium.

(U) During the initial phase of the investigation, the principal emphasis was on the behavior of wrought extruded tungsten. In laboratory experiments, hollow cylindrical specimens were subjected to controlled thermal environments which were comparable in severity and duration to those experienced by components in a solid rocket nozzle. Thermal, deformation and microstructural histories were measured in detail and compared with the results of analytical predictions.

(U) An existing computer program was modified to enable it to account for the stress reversals associated with thermal cycling. Preliminary results from the application of this analysis to the experimental results obtained in a single heating cycle of an extruded tungsten specimen gave excellent agreement between the measured and calculated final values of total circumferential strain at the I. D. and O. D. of the specimen.

(U) The tensile behavior of wrought tungsten has been studied from 2000°F to 5000°F at a nominal strain rate of 2 min.^{-1}. Tensile tests have been run attempting to duplicate the heating conditions in the thermal-stress experiments. Because microstructural changes are incomplete, the resultant stress-strain behavior differs from that normally observed, using slower heating rates.

(U) The first interim report under this contract will be published and distributed in January 1968.

(U) Application of Thompsine Tape to Solid Propellant Rocket Nozzles/ TRW, Inc. Equipment Labs/W. Winters/F04611-67-C-0051/ D.I. Thrasher (RPMCH)

(U) The technical effort was completed on 31 December 1967 and the final report is being reviewed. The TRW final report number will be AFRPL-TR-68-30.

(U) The objective of this program was to evaluate the effectiveness of Thompsine tape as an ablative material in solid rocket motor nozzles. The technical effort was divided into two phases.

(U) Phase I comprised preliminary evaluation of two styles of Thompsine tape chosen for a specific application; the low-cost nozzle of Contract AF 04(611)-11646 (Low-Cost Ablative Materials Evaluation Program, Aerojet-General Corporation) served as a model for tape design and application. Flat laminates of the two materials were prepared and tested to determine physical properties; oriented laminates were tested in the TRW solid simulator plasma jet facility to characterize the ablative performance. Limited tape-wrapping experiments were performed to evaluate the fabricability of each tape style.

(U) Phase II consisted of tape optimization, cost analysis, and the preparation of design criteria. The optimized tape was designed to provide maximum use of the material's capability in terms of erosion, char-through of the carbon-quartz interface, and backside structural-bond integrity in the model nozzle application. The physical properties were again evaluated for the optimized tape design; in addition thermal expansion coefficient, thermal diffusivity, and heat capacity were determined. More extensive plasma jet testing was performed, and the tape-wrapping fabricability was repeated. The hypothetical nozzle design was refined, and specifications for tape fabrication, impregnation, and tape-wrapping techniques were generated. A cost comparison was made between Thompsine tape nozzle components and conventional ablative components.

(U) Considering all factors affecting the final nozzle component costs (raw material production, impregnation, tape wrapping and billet processing, and machining) TRW found that Thompsine tape would result in a cost increase of about 30% in the hypothetical nozzle application. Since the use of Thompsine tape would result in a weight saving (5% of total nozzle weight), the 30% cost increase would result in an increase in payload capability for a rocket propulsion system. Whether Thompsine tape offers a potential overall advantage over conventional cloth tape could only be determined by a mission-oriented tradeoff analysis; such an analysis was beyond the scope of this contract. TRW's cost analysis was predicated on a high "quantity level" of tape usage (50,000 pounds); the cost increase would be markedly higher at lower quantity levels.

(U) Materials characterization data were much too extensive to present in this report. The TRW final report will present them in detail.

(U) Combustion Efficiency Investigation of High-Energy Solid Propellants/ Hercules ABL/Dr. R. Meyers/F04611-67-C-0052/Capt C.E. Payne (RPMCP)

(U) This program is nearing completion; the Final Report will be distributed during March 1968. The goals of this program are as follows:

a. Elucidation of combustion phenomena as related to the combustion efficiency of metal and metal hydride fuels.

b. Verification of laboratory measurements of combustion efficiency.

c. Development of an agglomeration combustion efficiency model.

d. Investigation of methods to improve the combustion efficiency of solid propellant metal/metal hydride additives.

(U) The confirmation of the laboratory method of characterizing combustion efficiency was done by the selection of previous motor firings which have sufficient firing data available to allow a calculation of the losses associated with combustion inefficiencies. Actual propellant samples were obtained where possible. In some cases the formulation was necessarily duplicated. Final evaluation of the laboratory method of determination of combustion efficiency is now being made.

(C) Methods of improvement of the combustion process of various thermogens have included the study of fluorinated plasticizers as an improvement method and the evaluation of thermogen oxidizer coatings. A wax coating method for beryllium hydride developed under last year's program allowed a decrease in mix viscosity and an increase in BeH_2 loading resulting in the highest delivered Isp for a solid propellant to that date.

(U) An agglomerate combustion model is presently being upgraded to include the results of this program. The model includes the consideration of metal/metal hydride agglomeration on the propellant surface as the primary deterrent to the attainment of maximum combustion efficiency. The agglomeration-ejection mechanism is thought to be collision with active sites. Active sites are combusting oxidizer particles.

(U) A Research Program on Solid Propellant Physical Behavior/ California Institute of Technology, Pasadena, California/ Dr. F.C. Lindvall/F04611-67-C-0057/Lt S.W. Beckwith (RPMCB)

(U) The objective of this program is to provide a greater understanding of the behavior of composite solid rocket propellants and to evaluate well-characterized cross-linked elastomeric materials. One of the major tasks will be to establish multiaxial testing techniques in order to define a failure surface in principal stress space and derive an associated failure criterion.

(U) The pressurized tensile tester (Ref. 1) was modified to reduce the pumping time from 30 to 15 minutes in order to allow a more rapid testing schedule. Tests have been conducted on SBR ring specimens at a cross-head speed of 1.40 inches per minute under pressures of 0, 500, 1000, 1500 and 2000 psi. These tests were carried out at room temperature using Arnold's Laboratory Safety Solvent No. 99 as the swelling and pressurizing liquid. A search was initiated for a confining liquid which will not swell rubberlike materials and will not dissolve inorganic fillers such as ammonium perchlorate or sodium chloride. At this time glycerol appears to be a likely candidate and tests are in progress to asses its suitability. Initial test results indicate that the elongation and nominal stress (based on the original cross-sectional area) increase slightly with the hydrostatic pressure. However, these data can be plotted on a Smith failure envelope.

(U) Investigation of the dynamic properties of a triblock copolymer, Shell's Kraton 102, was continued using a modified version of the GALCIT Torsion Pendulum. The loss tangent was measured over the temperature range of -50°C to over 100°C. The Kraton showed two damping peaks: one somewhere below -50°C, and the other at 85°C. A similar determination, made on a styrene-butadiene-styrene block copolymer of molecular weight 10,000-30,000-10,000 showed a lower peak at -30°C. The torsion pendulum was further modified to operate below the Tg of polybutadiene using liquid nitrogen.

(U) The torsion-tension apparatus was put into operation and calibrated using GALCIT I (Solithane 113). To our knowledge this is the first time uniaxial tests in both compression and extension have ever been carried out on the same specimen. The results, as isochronal stress-strain curves, are being used to examine current theories of large deformation behavior. Uniaxial stress-strain curves were obtained for two rubber specimens from ϵ = -17 to + 6.7%. The response seems to follow the simple behavior predicted by the kinetic theory of rubber elasticity from -10 to +7.5% strain in that plots of σ vs. $\lambda - \lambda^{-2}$ are linear in this range. The experimental error in the Mooney-Rivlin plot is too large in this range to assess the response. All of the data are reasonably well described by the Martin-Roth-Stiehler equation.

(U) Formulation studies on the Firestone Stereon 700 solution-polymerized SBR were continued in order to obtain an optimum formulation. The dicumyl peroxide and antioxidant contents were varied as were the cure times in order to control the functionality of the cross-linking process and to assess the relative effects of functionality and chain concentration on the tensile properties of the elastomer. Sol/gel ratios and Shore A hardness measurements have also been conducted to date. GALCIT I (Solithane 113) is being distributed for failure analysis studies on a limited basis to various researchers.

(U) The previous work interconversion (Ref. 1) was extended to include the approximations to the relaxation spectrum from loss and relaxation modulus data, and the approximations to the retardation spectrum from storage, loss, and creep compliance data. Improvements on the approximations calculated from relaxation modulus and creep compliance data by correcting the associated intensity functions is being pursued.

(U) REFERENCE

1. Landel, R. F., Tschoegl, N. W., AFRPL-TR-67-193, Volume I, June 1967, Third Annual Report, Contract AF 04(611)-9572, AD 822060.

(U) Supply of Solid Propellant Samples for the In-House Aging Program/ Thiokol Chemical Corporation, Wasatch Division, Utah/B. Williams/ F04611-67-C-0061/Lt A.E. Karabela (RPMCP)

(U) The purpose of this contract is to supply AFRPL with samples of two advanced composite propellant systems containing promising energetic oxidizers. The two oxidizers are hydrazinium diperchlorate (HP_2) and hydroxylamine perchiorate (HAP). In addition, samples of TPH-1011, an ammonium perchlorate propellant, will be obtained to serve as controls. These samples are to be used for the In-House Aging Program. Evaluation of aging characteristics will be made over a 3-year period. Approximately 300 pounds of propellant in the form of tensile specimens, $\frac{1}{2}$-gallon blocks, and 3-inch grains will be furnished. Work on this program commenced in July 1967 and has a target completion date of April 1968.

(U) Texture-Hardened Titanium Rocket Motor Case Development/ Lockheed Missiles and Space Corporation/J. Fitzpatrick/F04611-67-C-0074/Capt E. M. Schneider (RPMCH)

(U) Texture-hardened titanium is a titanium whose hexagonal close-packed crystal structure is preferentially aligned so that the crystal basal planes, and hence all slip direction, lie in the plane of the sheet. This means that thinning cannot occur due to slip if the sheet is subjected to biaxial tension such as exhibited in a pressure vessel or rocket motor case. Titanium strengths up to 300,000 psi and strength/density ratios of 1.5×10^6 inches can be predicted for an ideally textured heat-treatable titanium alloy. The strength density ratios of maraging steel and fiberglass are 1.0×10^6 and 1.7×10^6 inches respectively. A weight saving of 50% over conventional maraging steel cases can be predicted.

(U) The Contract F04611-67-C-0074 objective is to demonstrate the merit of a heat-treatable texture-hardened titanium alloy. The technical program will encompass the establishment of texture-hardened titanium processing parameters through laboratory material-property evaluations, heat-treatment optimization, weld studies and rocket motor case fabrication and hydrotesting.

(U) The effort in Phase I was toward the determination of suitable rolling and heat-treating procedures for development of favorable textures in one or both of two alloys: Ti-6A1-4V and Ti-7A1-2.5 Mo. The work comprised the following aspects: rolling and heat-treating trials; identification of textures through measurements of associated anisotropic mechanical properties; determination of facture toughness indices; texture characterization through pole figure analyses and optical metallography; and analytical study to develop methods of predicting the mechanical behavior of pressure vessels fabricated from textured alloys. The lateral strain ratio R has been used for the purpose of assessing biaxial strength by calculations based on the anisotropic plasticity theory of R. Hill.

(U) The Phase I effort is reported in detail in AFRPL-TR-67-302, AD 824691. Although the yield strength-to-density ratio of 1.5×10^6 in. was not achieved, a yield strength-to-density ratio of 1.4×10^6 has been demonstrated for Ti-6Al-4V, round-rolled. It may be possible to obtain higher calculated biaxial yield strengths in Ti-7Al-2.5 Mo by aging at higher temperatures.

(U) The subsequent program phases are investigating texture-hardened weldments and texture-hardened pressure vessel fabrication. Hydroburst of 18-inch-diameter cylinders will provide demonstration of the concept feasibility.

(U) High-Performance Shrouded-Rocket Tests/Martin Marietta Corporation (Denver Division)/R. L. Chapman/F04611-67-C-0077/ Lt D.J. Davis (RPMMM)

(C) This high-performance shrouded-rocket test program was initiated to conduct a shrouded-rocket combustor configuration optimization using a fuel-rich, baseline, aluminum propellant. The program objective was to deliver a net specific impulse of over 450 seconds at air-to-fuel ratios less than 10 when operating between simulated Mach numbers of 2 and 3 under direct-connect test conditions.

(C) Phase I consisted of design and fabrication of the test model hardware. The test model was designed for best performance between Mach 2 and 3 from sea level to 50,000 feet altitude. The system design represented a propulsion system with four aft-mounted scoop inlets with an external compression ramp and boundary layer diverter. Two rocket motor configurations were tested, one with five parallel nozzles and one with four canted toward the centerline. The nozzles for both configurations were arranged with one on the centerline and four peripheral nozzles. Eighteen direct-connect test firings were conducted at the Ordnance Aerophysics Laboratory, Daingerfield, Texas. Five test firings were accomplished with the 16% aluminum propellant and the remainder with the fuel-rich 35% aluminum propellant. The data was reduced for three inlet designs with design points of Mach 2.0, 2.5, and 3.0, and a "rubber" inlet that operates critical at all flight conditions. An excess of 450 seconds of specific impulse was achieved at Mach numbers from 2.0 to 3.0 and sea level to 35,000 feet.

(U) The technical effort under this contract has been completed. The final report (AFRPL-TR-68-4) is scheduled for distribution in February 1968. Previous shrouded-rocket development is detailed in the following references:

1. "Experimental and Theoretical Investigation of the Rocket Engine-Nozzle Ejector (RENE) Propulsion System," April 1965, AFRPL-TR-65-66 (C), AD 359763.

2. "Analytical and Experimental Investigation of Air-Augmented Rockets to Determine Thrust Minus Drag," Quarterly Progress Report, January 1966 AFRPL-TR-65-229 (C), AD 368314; March 1966 AFRPL-TR-66-31 (C), AD 370515; June 1966 AFRPL-TR-66-172 (C), AD 486640.

3. "Simulated Altitude Performance of Air-Augmented Solid Propellant Rocket Motors," Part I Oct 66 AEDC-TR-66-157 (C), AD 376087; Part II Oct 66 AEDC-TR-66-172 (C), AD 376743.

4. "Performance Characteristics of an Air-Augmented Solid Propellant Rocket at Mach numbers of 0, 0.31, and 0.50," December 1966, AEDC-TR-66-245 (C), AD 377978.

5. "Performance Characteristics of an Air-Augmented Solid Propellant Rocket at Mach Numbers of 0.59, 0.74, 0.90, and 1.18," March 1967, AEDC-TR-67-39 (C), AD 379587.

6. "Analytical and Experimental Investigation of Air-Augmented Rockets to Determine Thrust Minus Drag," Final Report, July 1967, AFRPL-TR-67-166 (C). AD numbers: Vol I-383062; Vol II, Pt 1-383063; Pt 2-383064; Vol III-383065; Vol IV, Pt 1-383066; Pt 2-383067.

(U) Demonstration of a Solid Propellant Postboost Propulsion System (PBPS)/Thiokol Chemical Corp./P. Nance/F04611-67-C-0080/ R. Felix (RPMMA)

(C) The objective of this program is to demonstrate the capability of an all-solid (two chamber) system to provide precise postboost thrust and attitude control for a 10- to 15-min. duty cycle. Successful demonstration of this capability will establish the feasibility of incorporating an all-solid propellant postboost propulsion system (PBPS) into future weapon systems.

(U) The propulsion system consists of an axial thrust motor with a vectoring nozzle, a gas generator, an attitude-control system (ACS) with roll control, and the asscciated warm gas distribution system. The PBPS design summary is shown in Table I.

(U) A full-scale gas generator was successfully static-tested at TCC on 21 December 1967 at ambient conditions. The primary objective of the test was to demonstrate the functional capability and survivability of the interchamber valve, attitude-control valve, pressure regulator and thrusters, verify gas generator propellant performance and to demonstrate performance of the closed-loop control system. All major test objectives were achieved. The internal gas generator ballistics are shown below:

(C) Internal Ballistics Performance

Parameter	Predicted	Actual
P_{avg} (psia-high level)	780	780
P_{avg} (psia-low level)	150	150
Duration (sec)	804	905

(C) A complete system sea-level test was successfully performed on 25 January 1968. The primary objectives of the test were to verify axial motor performance, and demonstrate the survivability of the submerged gimbaled nozzle. The motor was programmed to pulse 20 times for a total test duration of 545 seconds. The motor reignited after the thirteenth pulse. Cause of reignition is attributed to sea-level conditions (ambient pressure preventing hot gases from exhausting and allowing insulation to burn) and excessive radiation from nozzle plastic components and insulation. Design changes are being considered to reduce possibility of reignition during the altitude test. The nozzle and ACS components performed as predicted.

(U) The first of four PBPS altitude tests is scheduled for early March at the AFRPL Altitude Facility.

TABLE I

(C) BASIC PROPULSION SYSTEM DESIGN SUMMARY

Axial Motor		
Axial Motor Pulses		31
Minimum Delivered Axial Impulse, lb-sec		500,000
Average Thrust, lbs		4,200
Average Pressure, psia		200
Burning Time, sec		119
Burning Rate, in/sec		0.110
Vac. Specific Impulse, lb-sec/lb		268
TVC Vector Angle, degrees		15
Propellant Weight, lbs		1451

Gas Generator	Axial Thrust Mode	ACS Mode
Average Pressure, psia	780	150
Burn Time, sec	119	781
Burn Rate, in/sec	121	.037
Propellant Weight, lbs	1433	

Attitude Control System		
Pitch and Yaw Thrust, lb_f	(4 each)	50
Roll Thrust, lb_f	(8 each)	10
Minimum Impulse Bit (lb-sec)		
Pitch and Yaw		.4 ±10%
Roll		.2 ±10%

(U) Investigation of Aerothermodynamic Control of the Shrouded-Rocket Cycle/United Aircraft Research Laboratories/R. L. O'Brien/ F04611-67-C-0082/Lt H. Joonsar (RPMMM)

(U) The objective of this program is to conduct an analytical investigation of the performance and stability of the air-augmented shrouded rocket cycle. Conclusion of the program will result in identifying those methods of aerothermodynamic control which will permit high levels of cycle performance to be obtained throughout a wide range of Mach numbers and altitudes.

(C) The baseline configuration for this study is a shrouded design with L/D = 1.2 and an exit-to-combustor area ratio of 1.5. An aft-mounted, annular, external compression inlet with a design point of Mach 3 and 40,000 feet will deliver the air to the secondary combustion chamber. The baseline primary utilizes 16% Al, AP, PBAN propellant at a primary chamber pressure of 1000 psia.

(U) The baseline configuration will be altered by individually varying the inlet-diffuser pressure recovery, shroud geometry, heat addition, and primary rocket conditions at selected points on the trajectory map. Performance will be determined for these altered configurations.

(U) Other types of inlets that will be analyzed are: (1) a series of external compression inlets which incorporate an isentropic surface and are designed to operate critically at each flight condition; and, (2) a variable-geometry external compression inlet which incorporates a slideable, expandable ramp or a variable-geometry mixed-compression configuration employing a slideable cowl. The inlet performance will not include the effects of vehicle forebody boundary layer or the angle-of-attack effects.

(U) An ejector analysis will be conducted to determine shroud-nozzle performance for two shroud geometries and realistic heat-release rates. The configurations are: (1) cylindrical-divergent (baseline); (2) cylindrical convergent-divergent (variable and fixed); and (3) divergent. The area ratios to be investigated will be between .75 and 3.0. Realistic heat-release rates will be determined by employing Martin Company experimental data obtained under Air Force contracts along with the United Aircraft Corporation Research Laboratories' (UARL) mixing-combustion computer program.

(U) The effect of varying the primary rocket exhaust properties will also be investigated. Primary rocket flow rates from 5.0 to 25.0 lb/sec, chamber pressures between 500 to 2500 psia, and expansion ratios from 1.5 to 10 will all be looked at during the course of this program.

(U) The program will include trade-off studies to determine cycle performance in terms of fuel specific impulse and thrust coefficient and parameter sensitivity. The program will identify the effective limits of each parameter on cycle control within the limits of the trajectory map.

(C) Progress: The work that has been accomplished or initiated to date is the following: (1) determining the detailed composition of the primary rocket propellant, the result of which was that the only fuels which must be considered for secondary combustion are carbon monoxide and hydrogen; (2) selection of the baseline trajectory for the engine performance calculations and supersonic performance calculations for the baseline inlet up to Mach 4.0. This performance is presented as relative weight flow and pressure recovery as a function of Mach number; (3) all computer programs that are required for this study have been modified and checked out; (4) realistic combustion efficiency and heat-release rates for use in the generalized ejector computer program, for some cases, as well as

information concerning combustor static pressure distribution and velocity, temperature and concentration profile nonuniformities, have been obtained by using the UARL mixing-combustion computer program; and (5) the ejector characteristics for the two shroud configurations have been determined. This is presented as pressure ratio and relative weight flow. Superimposing the inlet characteristics would indicate the inlet-ejector match point. Performance of the rocket has not been determined but the convergent-divergent shroud has the better matching characteristic with respect to the inlet. The indication has been that it is quite hard to choke the secondary flow unless a physical throat is incorporated.

(U) The experimental data being used to correlate the analytical model is being taken from the following references:

1. "Experimental and Theoretical Investigation of the Rocket Engine-Nozzle Ejector (RENE) Propulsion System," April 1965, AFRPL-TR-65-66 (C), AD 359763.

2. "Analytical and Experimental Investigation of Air-Augmented Rockets to Determine Thrust Minus Drag," Quarterly Progress Report, January 1966 AFRPL-TR-65-229 (C), AD 368314; March 1966 AFRPL-TR-66-31 (C), AD 370515; June 1966 AFRPL-TR-66-172 (C), AD 486640.

3. "Analytical and Experimental Investigation of Air-Augmented Rockets to Determine Thrust Minus Drag," Final Report, July 1967, AFRPL-TR-67-166 (C). AD numbers: Vol I-383062; Vol II, Pt 1-383063; Pt 2-383064; Vol III-383065; Vol IV, Pt 1-383066, Pt 2-383067.

(U) Igr.iter Design Handbook for Solid Propellant Rocket Motors/ CETEC Corp./C. Falkner/F04611-67-C-0083/Capt C.E. Payne (RPMCP)

(U) This is an analytical program with the goal of providing a handbook to allow the scientific design of solid propellant ignition systems. The program will correlate the experimental data which has been developed on ignition research programs.

(U) The literature survey has been completed and data correlation is now being effected. In addition to a design handbook, a computer program will be provided. When provided with motor geometry, igniter and motor propellant thermodynamic information, and propellant ignition delay properties, the computer program will predict the pressurization rate for the motor. Plots of surface area ignited, surface temperature, and pressure/time relationship are provided as an output from the computer.

(U) The basic deficiency of the ignition information available is with regard to heat transfer from the igniter gas to the surface during the flame spread interval. Additionally, experimental data relative to pyrotechnic igniters is very scarce. It is very difficult to predict burning area versus time and burn rate of pellet-type igniters. However, a useful computer program will be provided which will considerably reduce the amount of experimental data required for the design of a new igniter system.

(U) Compilation of Gaseous Injection Analytical Techniques/ Aerotherm Corporation, Palo Alto, Calif./T.J. Dahm/ F04611-67-C-0086/Capt D. Stump (RPMCH)

(U) The program consisted of the compilation of all the analytical techniques developed by Aerotherm (formerly Vidya) in support of Contracts AF 04(611)-7444 and AF 04(611)-9066. The effort consisted of collecting all the analytical techniques developed and proven by both of the analytical models used in these large and small motor tests. The analyses were generalized for arbitrary gases and presented in a manner that can be used by engineers either as a preliminary design tool or for final system optimization.

(U) The Final Report No. 67-11, AFRPL-TR-67-169, was published 1 July 1967, AD 817962.

(U) Development of an Energetic Propellant with Hydroxylamine Perchlorate/Thiokol Chemical Company - Elkton Division/ Dr. C. Alfieri/F04611-67-C-0088/R.C. Miller (RPMCP)

(C) This effort is to demonstrate a feasible propellant containing HAP, (hydroxylamine perchlorate) in an energetic binder. Of particular importance is obtaining good reproducible cures and adequate stability.

(C) The primary approach in this program was the examination of a variety of hydroxyl-terminated polyethers with a variety of isocyanate curatives. The plasticizer was to be selected from a group of liquid nitrocompounds. Early in the program considerable difficulty was experienced with the compatibility of binder ingredients with HAP. A more careful look resulted in the discovery that several of these "dry" ingredients were indeed quite "wet" for this use. Once these ingredients were properly dried these problems were much reduced. The gassing of propellants was still noticed but due to the exceptionally short pot life of this system it might be ascribed to poor degassing of the propellant mix. Eventually a difunctional isocyanate based on isophorone, IPDI, was found to increase pot life to several hours and to decrease the apparent gassing. This effort essentially completed Phase I effort and a Phase Report has been distributed.

(C) The scale-up formulation which will be characterized in Phase II contains FEFO (a fluoronitroplasticizer), IPDI (the curative - a trifunctional polyether), HAP, and AlH_3. In Phase III TVOPA will be examined in this system. Theoretical Isp values over 280 will be demonstrated.

(U) Combustion-Tailoring Criteria for Solid Propellant Rockets/ Lockheed Propulsion Company/N. Cohen/F04611-67-C-0089/ Capt C. E. Payne (RPMCP)

(U) The objective of this program is to attempt to bridge the gap between the combustion research scientist and the practical goals of the propellant formulator. Much solid propellant combustion research is directed toward phenomena which are in many cases not applicable to the realm of practical interests. In this program practical, tractable combustion-tailoring criteria are being sought.

(U) The combustion of solid propellants is being investigated in a research device which represents as nearly as possible the actual environment which occurs in an operational motor. The test motor (a heavyweight device with opposing slabs of propellant) is heavily instrumented in order to provide a maximum of information. Parameters which are being monitored include: pressure, temperature profiles, heat transfer (radiative and convective), particle trajectories, surface phenomena (high-speed photography), exhaust species, and reaction kinetic constants.

(U) The program phases consist of equipment development, checkout with well-characterized propellants, evaluation of advanced solid propellant systems, and the development of tailoring criteria. The program is in the first-year period and the equipment is currently being checked out.

(U) Carbides for Solid Propellant Nozzle Systems/TRW, Inc., Equipment Labs./D. Laverty/F04611-67-C-0094/Capt E. M. Schneider (RPMCH)

(U) The objective of this program is to establish the magnitude of the chemical reactivity problem between Al_2O_3 and carbide composites being considered for rocket nozzle throat materials. A secondary objective is to establish the validity of low-cost laboratory tests as a tool for evaluating nozzle throat material potential performance.

(U) This program will subject an advanced Tantalum carbide hyper-eutectic material and a tantalum-hafnium-carbon alloy to a high-temperature plasma jet. The plasma jet has a heat flux of 1200 BTU/ ft^2/sec. Specimen temperatures are brought up to typical flame-liner surface operating temperatures by resistance heating. The plasma jet injects molten alumina (Al_2O_3) on the specimen to measure the effects of alumina on nozzle mechanical erosion. Static chemical reactivity will be evaluated by a sessile drop test wherein the carbide materials are heated to 4500°F or higher in contact with molten Al_2O_3. The laboratory test effectiveness will be determined by predicting nozzle performance on a demonstration test to be conducted under Contract AF 04(611)-11608, Aerojet-General Corporation. The predicted values will be based on plasma-jet and sessile-drop test results.

(U) Plasma-jet tests have been conducted on the microcomposite specimens. In general, the erosion resistance of the microcomposite materials in the plasma jet is comparable to that of stoichiometric HfC at temperatures of 5400°F and higher. Below this temperature, the microcomposite has a somewhat lower erosion rate. Results indicate a threshold temperature between 5400 and 5600°F above which the carbide recession rate increases rapidly. The mechanism responsible for the accelerated erosion rate appears to be eutectic reaction between the liquid alumina particles and hafnium in the microcomposite.

(U) Future work will include sessile-drop tests and plasma-jet tests on the TaC-C hypereutectic material. Performance prediction of the Aerojet demonstration nozzles should be completed by March 1968.

(U) Development of a Very Highly Efficient High-Energy Propellant/ United Technology Center/P. Allen/F04611-67-C-0096/R.C. Miller (RPMCP)

(C) The objective of this program was to demonstrate that AlH_3 propellants formulated with difluoramino binders (i.e., PBEP TVOPA mixtures) will offer much improved performance partially through increased theoretical Isp but particularly through increased Isp efficiency. In order to achieve this task, reliable cure and processing must be achieved.

(C) The primary problem to date has centered on obtaining adequate cure of PBEP. A partial list of significant variables contributing to the difficulty of overcoming this problem follows: PBEP lot, completeness of solvent removal, PBEP functionality, equivalence ratio, diol to triol ratio, curative type, catalyst type, catalyst concentration, mix size, mix duration, sample configuration during cure, fuel characteristics (AN treatment or not).

(C) The program has been hampered by inconsistent results from which we may infer that a vital variable is not being controlled. To prevent the lot-to-lot variation from further complicating the problem, a master batch of PBEP will be blended from several reactor runs.

(C) Despite the cure difficulties, a series of 1-lb motors has been fired. The efficiencies noted were above conventional formulations but below aluminum metal, PBEP propellants. A series of 4-lb motors is in preparation.

(U) Solid Propellant Structural Test Vehicle, Systems Analysis and Cumulative Damage Program/Lockheed Propulsion Company/ J. W. Jones/F04611-67-C-0100/Lt S. W. Beckwith (RPMCB)

(U) Solid Propellant Cumulative Damage Program/Aerojet-General Corporation, Sacramento/K. W. Bills/F04611-67-C-0102/ D. Saylak (RPMCB)

(U) Solid Propellant Cumulative Damage Program/Rocketdyne, McGregor Division/C. E. Bryant/F04611-67-C-0103/D. Saylak (RPMCB)

(U) These three programs are part of an integrated Structural Test Vehicle - Cumulative Damage effort. The University of Utah (F04611-67-C-0042), Atlantic Research Corporation (F04611-67-C-0015), and AFRPL In-House (Mechanical Behavior, Project 305902 AMF) are also contributing to the effort (Ref. 1). The prime responsibility for the design and development of a structural test vehicle was awarded to Lockheed Propulsion Company. To date, three highly filled (86.5%) CTPB propellant STV's have been designed and manufactured (Ref. 2). These motors are 7 inches in diameter by 35 inches in length with simple, circular port grains. The motors currently employ five types of transducers in addition to the thermocouples:

(1) Through-case Shear Stress Gage - VDC Model F40A

(2) Through-case Tensile-Compressive Stress Gages - VDC Model F41A

(3) Low-Compliance Miniature Diaphragm Gages - EOS Model 1017-0024

(4) High-Compliance Miniature Diaphragm Gages - EOS Model 1017-0023

(5) Semi-Conductor Strain Gage Cubes

A 4,000-pound batch of LPC 0064-61E STV propellant was manufactured and cast into the STV's and into containers for delivery to the associate contractors. Preliminary JANAF tests were conducted to determine

the failure envelope and stress relaxation modulus. A lateral-strain measuring device for uniaxial tensile tests has been made, calibrated and used on propellant tests. Preliminary tests show volumetric changes at failure in the range of 10 to 20%. Designs and methods for casting two Solithane 113 (GALCIT I Interim Standard - Ref. 3) STV's have been formulated. These motors will serve as a control because the material is a well-characterized linear viscoelastic material.

(U) Aerojet-General Corporation has been studying the effect of filler reinforcement on the mechanical properties of composites in general. Tests to date show that the stress concentration in the matrix, decreasing with increasing filler content, is responsible for the internal tearing of the polymer. Photographic and birefringence studies of large glass beads in rubber matrices were continued. Two areas of investigation were pursued: (1) failure mechanisms after dewetting; and (2) comparisons of failure mechanisms in simple versus repeated or sequence loading steps. Rapid surface oxidation was demonstrated with constant load tests after three periods of exposure to the atmosphere. The best representation of the time to failure appears to be:

$$N\ (t) = No e^{-k}\ (t - t_c)$$

where N(t) is the number of specimens remaining unbroken at time t

No is original number of specimens

t is time

k is the constant

t_c is the time of first failure

Shore A hardness measurements were determined for storage treatment at 180°F.

(U) Single environment tests have been conducted at Rocketdyne in the triaxial stress state on the STV propellant. Because of the magnitude of the strains involved, it was necessary to determine the stiffness of the Instron machine (and linkage) used in conducting the tests. It was concluded that the conditions imposed on the poker-chip specimen are most accurately described as "stress prescribed boundary" conditions. The analytical derivation of the equations necessary for the solution of a spherical (triaxial tests) and cylindrical (biaxial tests) flaw in a uniform plane stress or strain field were completed for various loading conditions, e.g., constant strain rate. These will be applied to flaw instability concepts as developed in a series of papers by Williams (Ref. 4, 5, 6).

(U) Work was initiated at Rocketdyne, Canoga Park, to provide photomicrographs of the surface of a failing or cracking propellant following a constant stress-rate-loading history. Small hollow cylinders with either a cast or machined surface are pressurized internally to failure at a rate of 90 psi/min. Preliminary tests indicate different failure mechanisms in the two surfaces.

(U) REFERENCES

1. Saylak, D., "Air Force Solid Propellant Mechanical Behavior and Structural Analysis Programs", Bulletin 6th Annual ICRPG Working Group on Mechanical Behavior, December 1967.

2. Lockheed Propulsion Company, "Special Report No. 1, Solid Propellant Structural Test Vehicle, Systems Analysis, and Cumulative Damage Program," LPC 8385-1, Redlands, California, 13 Oct 1967.

3. Knauss, W.G., "A Cross-Linked Polymer Standard; Report on Polymer Selection," First Annual Report, AFRPL-TR-65-111, April 1965, AD 616698.

4. Williams, M.L., "The Fracture of Viscoelastic Materials," Fracture of Solids, Interscience Publishers, New York, 1963.

5. Williams, M.L., "The Initiation and Growth of Viscoelastic Fracture," International Journal of Fracture Mechanics, Vol. 1 No. 4, 1965.

6. Williams, M. L., "Fatigue Fracture Growth in Linearly Viscoelastic Materials," UTEC SM66-003A, University of Utah, June 1966.

(U) Development and Demonstration of an Improved Rocket for the Flechette Warhead/Aerojet-General Corp., Sacramento, Calif./ T. Bowden/F04611-67-C-0114/L. G. Meyer (RPMMA)

(C) The objective of this program is to develop an improved 2.75-inch-diameter rocket which will provide the performance required for effective delivery of a flechette warhead from tactical aircraft. As a minimum, the rocket must provide powered flight for 5000 ft with a burnout velocity of 3600 ft/sec when launched from an aircraft traveling at 750 ft/sec in a 30° dive angle. The program scope includes rocket design, aerodynamic analysis and testing, propellant tailoring, manufacturing, motor test through Preliminary Flight Rating Tests (PFRT) and delivery of 380 units to the Air Force.

(U) The improved 2.75-inch rocket retains the present 2.75-inch design and hardware with the following modifications:

1. A cast-in-case composite PBAN (polybutadiene acrylonitrile) propellant.

2. Partially case-bonded propellant grain.

3. Increased volumetric loading.

4. Modified nozzles to accommodate higher flame temperature propellants.

5. Aft-end pellet igniter.

6. Fins skewed to achieve a spin rate of 5 revolutions per second to provide flight stability.

(U) Eleven of the 39 development motors have been fired. Of these, six successful firings have been conducted. Three of the failures were due to poor materials, instrumentation and an oversized chamber. These failures are not considered to be the result of major problems, and corrections have been made to prevent recurrence. Two motors failed at -65°F due to poor grain-release methods. A change in grain release was instituted. Nozzles, aft-chamber insulation, and the ignition system are functioning well and the desired ballistic properties of the propellant have been obtained.

(U) In addition to the development motor tests, six motors will be tested at the Langley Research Center to determine the motor's capability to withstand high longitudinal acceleration and spin. An additional six motors are to be shipped to Eglin AFB, Florida in January for ground-launched flight tests to determine launcher survivability, burnout velocity and accuracy.

(U) Following the above tests, the design will be frozen and 45 Preliminary Flight Rating Tests (PFRT) will be conducted under the air-launched environment. The program will be completed with the shipment of 380 rockets to Eglin AFB for ground and aircraft-launched flight tests. The Air Force will have an option on a production buy of 300,000 units to be produced over a 12-month time period.

(U) Deviation Nozzle Program/Aerojet-General Corporation, Sacramento/ J. Warga/F04611-67-C-0117/W. F. Payne (RPMCH)

(U) This program will evaluate a submerged nozzle on a surplus second-stage Minuteman motor under AFRPL Project NOMAD. The nozzle is constructed similar to the Stage 0 Titan III nozzle and employs the same materials. The plastic components were designed to represent off-specification manufacturing practice and evaluate the effects of physical defects on actual performance. The data will be useful to establish reasonable acceptance-rejection criteria of Materials Review Board actions in the Titan program.

(U) The nozzle configuration and instrumentation (in-depth thermocouples) are identical to the test nozzles employed in the Low Cost Ablative Program (AFRPL-TR-67-310) and the Ablative Process Parameters Program (AFRPL-TR-68-29).

(U) The nozzle will be delivered to AFRPL for firing during January 1968. The final report will be distributed in May 1968.

(U) Supply of Solid Propellant Samples for the In-House Aging Program/ United Technology Center, Sunnyvale, California/M. Widlock/ F04700-67-C-0517/Lt A. E. Karabela (RPMCP)

(U) The purpose of this contract is to supply AFRPL with samples of an advanced composite propellant system containing aluminum hydride (AlH_3). In addition, a control formulation will be supplied containing aluminum (Al) fuel. These propellant samples are to be used for the In-House Aging Program. Evaluation of aging characteristics will be made over a 3-year period. Approximately 500 pounds of propellant in the form of disks, hemispheres, tensile specimens, $\frac{1}{2}$-gallon blocks, 3-inch grains, and 15-pound grains will be furnished. Work on this program commenced in August 1967 and has a target completion date of May 1968.

(U) Air-Launch Single-Chamber Controllable Solid Rocket Motor/Aerojet-General Corp., Sacramento, Calif./C. T. Levinsky/F04611-68-C-0003/R. E. Smith (RPMMA)

(U) The objective of this program is to demonstrate a single chamber solid propellant motor capable of throttling and operating under air-launch motor environmental conditions. A secondary objective will be to demonstrate a thrust-vector-control system for the single-chamber motor.

(U) Work on this contract started in September 1967. As of December the design has been completed and hardware for the first motor ordered. A propellant formulation was selected and scale-up to 2000-lb batch was initiated. The first motor is scheduled for testing during April 1968.

(U) Flexible Exit Cone Nozzle Development Program/Thiokol Chemical Corporation/K. Northness/F04611-68-C-0004/Capt D. Stump (RPMCH)

(U) This program will develop and demonstrate a new thrust-vector-control (TVC) nozzle concept for improved solid rocket system performance and reliability. The new concept (TVC) consists of replacing a section of the nozzle exit cone with a flexible joint which will permit vectoring of the supersonic section of the exit cone.

(U) Cold-flow facility modifications have been completed and checkout is in process. Cold-flow models are designed and are being fabricated.

(U) The first 10 TU-379 (subscale) elastomeric material evaluation motors have been tested and analysis of the data is being completed.

(U) The elastomer-composite joint bonding and physical property tests are complete and data is being evaluated.

(U) The three 3.8-inch-throat-diameter material-evaluation nozzle tests are scheduled to be accomplished at the Air Force Rocket Propulsion Laboratory's Char Motor Facility during May 1968. The two demonstration nozzles are scheduled for testing during September 1968 on the 40-inch six-component thrust stand at the AFRPL Char Motor Facility.

(U) Photoelastic Investigation of Rocket Grain Stresses/Mathematical Sciences Northwest, inc., Seattle, Wash./Dr. M.E. Fourney/ F04611-68-C-0013/Lt C.D. Smith (RPMMD)

(U) The objectives of this study are:

1. To perform a computer verification of the results of Contract AF 04(611)-10529 (Mathematical Sciences) using up-dated case-propellant stiffness ratios.

2. To conduct a photoelastic study of axisymmetric grain designs, present the data in suitable handbook form, and verify the data by computer.

(U) The go-ahead date on this 12-month program was 24 July 1967. The contractor has completed Task I, Computer Verification. The results appeared favorable. Task II, Testing, has begun.

REFERENCES

1. Becker and Brisbane, "Application of the Finite Element Method to Stress Analysis of Solid Propellant Rocket Grains," Volumes I, II, and III, Rohm and Haas, Report No. S-76, Contracts DA-01-021 ORD-12341(Z) and DA-01-021 AMC-11536 (Z), November 1965.

2. Fourney and Parameter, "Parametric Study of Rocket Grain Configurations by Photoelastic Analysis," AFSC Report No. AFRPL-TR-66-52, Mathematical Sciences, Corporation Report No. 65-29-12, Contract AF 04(611)-10529, March 1966, AD 480516.

3. Durelli and Lake, "Device for Applying Uniform Loading to Boundaries of Complicated Shape," Proceedings of the Society for Experimental Stress Analysis, Volume II, No. 1, 1953.

4. Williams, Blatz, and Shapery, "Fundamental Studies Relating to Systems Analysis of Solid Propellants," GALCIT SM 61-5, California Institute of Technology, 1961.

(U) Effect of Grain Shape on Stress Concentrations at the Case-Propellant Interface/Atlantic Research Corporation/C. N. Robinson/ F04611-68-C-0015/Lt C. D. Smith (RPMMD)

(U) The objective of this program is to demonstrate the structural advantages resulting from the use of a shaped grain-end design.

(U) Photoelastic studies conducted in Contract AF 04(611)-10378, Catholic University, have shown that propellant stresses at the grain end can be significantly reduced by use of a properly shaped grain end design. In fact, in some cases the need for a boot flap is eliminated.

(U) This 12-month program consists of three phases:

1. Photoelastic Analysis and Propellant Selection. Catholic University, as subcontractor, will investigate a wider range of grain end shapes than considered in the previous contract. Also included in this phase will be the selection of the propellant to be used in motor testing. Basically, this consists of choosing between PBAN and CTPB-type propellants. Factors to be considered are low temperature properties, reproducibility, and linearity.

2. Subscale Motor Testing. In this phase, small subscale laboratory motors will be cast with the selected propellant. The grain end design used will be based on the results of the photoelastic analysis of Phase I. These motors will be cooled in a stepwise manner until failure occurs. The behavior of the grain will be monitored both visually and by X-ray and will be correlated with existing theory.

3. Full-scale Motor Demonstration. A high web-fraction 12-inch-diameter motor will be cast using the most promising grain end design determined in Phase II. This motor will be thermally loaded and monitored as in Phase II. It is anticipated that this motor will have a low-temperature capability equal to, or exceeding, that of comparable motors with boot-flap designs.

(U) REFERENCE

Bulletin of the 5th Meeting, ICRPG Working Group on Mechanical Behavior, CPIA Publication No. 119, Vol 1, Oct 1966.

(U) Demonstration of Freon-Treated Motors/Rocketdyne, McGregor Division/C.E. Bryant/F04611-68-C-0017/D. Saylak (RPMCB)

(U) The objective of this program is to demonstrate the potential of a stress-relief technique to extend the environmental capability of an advanced state-of-the-art propellant. This program consists of an experimental study of the beneficial effects which can be derived by selectively dewetting a solid propellant grain with Freon-12. The improvement in crack resistance of the motor will be investigated under a combined thermal-vibrational loading condition.

(U) The Rocketdyne program consists of a two-motor demonstration program utilizing available Mk 38 SPARROW hardware (8 inches diameter, approximately 40 inches length) with the extended environmental propellant (Ref. 1). A new mandrel will be utilized providing a case-bonded cylindrical grain having an 80% web fraction and a high enough length-to-diameter ratio to ensure a "plane strain" stress state at the center of the grain. The environmental testing of the motors includes low-temperature excursions and vibration to define the failure threshold and an alternate motor which can be either hot-aged or fired. Motor No. 1 is a control round (grain will not be treated with Freon) to define the failure point of the basic propellant grain when subjected to incremental decreases in temperature with intermittent vibration. Motor No. 2 will include the Thiokol-developed stress-relieving treatment and then be subjected to incremental decreases in temperature with intermittent vibration to define its failure point.

(U) At the writing of this report, both of the tests have been completed. The results are being analyzed and will be reported in the next report.

(U) REFERENCES

1. "Solid Propellant Extended Environmental Capability Evaluation Program," January 1967, AFRPL-TR-67-22, AD 378580.

2. "Solid Propellant Extended Environmental Capability Evaluation Program," April 1967, AFRPL-TR-67-102, AD 381232.

(U) Effects of the Interaction of High-Frequency Sound Waves and Electromagnetic Radiation on Polymers and Rubbers/University of Oregon, Eugene, Oregon/Dr. W. L. Peticolas/F04611-68-C-0019/ D. Saylak (RPMCB)

(U) The objective of this program is to provide an understanding of photon-generated sonic rupture in plastics and rubbers. The program consists of an experimental and theoretical study of hypersonic waves in polymeric materials, using lasers as a source of electromagnetic radiation.

(U) Initial measurements will consist of the frequency and polarization of the scattered light as a function of the scattering angle. From these measurements at temperatures above and below the glass transition temperature of the polymer, the velocity and mode structure of sound waves will be determined. The molecular motion of the polymer molecules will also be probed, taking advantage of systematic changes in polymer type.

(U) In addition to the determination of sound-wave properties, a study of photon-phonon induced fracture will be instigated. A ruby laser will be used to produce multivibrational excitation of optical phonons as well as stimulated Brillouin Scattering. Various samples will be placed in the ESR (Electron Spin Resonance) cavity and fracture waves will be generated by ruby laser irradiation. Those chemical structures will be identified which exhibit weak link characteristics when subjected to electromagnetically induced fracture waves.

(U) No significant results have been obtained, since the program was just initiated and is in a buildup phase.

(U) Ballistic Test, Evaluation and Scaling (BATES)/Project 305901AMD/ C.W. Beckman, Lt L. Altman and TSgt T.H. Norton (RPMCP)

(U) Ballistic Test, Evaluation and Scaling (BATES) is an investigation of various parameters which can account for loss in performance of solid rocket motors and the determination of comparable data on the performance of other solid rocket motors. The objectives of this project are: (1) the development of a specific impulse scaling technique; and (2) support of the Air Force and government agencies requiring ballistic evaluation of solid propellants.

(U) During this reporting period, several milestones of the BATES program were realized. The milestones were: (1) completion of the 70-pound test motor calorimeter and initiation of firings; (2) initiation of L* studies with a double-length motor configuration; (3) initiation of firings utilizing a submerged-nozzle configuration; (4) completion of buildup for determining the effect of varying chamber pressure; and (5) starting checkout of a two-dimensional two-phase-flow computer program.

(U) A test program has been initiated to determine the effects of chamber pressure, metal loading, and nozzle geometry on heat loss. The program will utilize the 70-pound and 15-pound test motors.

(U) Seventeen support firings were conducted during this period. The formulations fired for evaluation were Aerojet's ANB-3238 and Hercules' VID, both toxic formulations. The VID formulation was also evaluated at Arnold Engineering Development Center for altitude characteristics. Checkout firings were conducted for the double-length chamber motor and the 70-pound test motor calorimeter.

(U) Exhaust plumes sampled were a Thiokol 120-inch motor, a Poseidon 2nd stage and BATES test firings in continuing AFRPL's large motor exhaust sampling program. In conjunction with the two-phase-flow effort,

a one-dimensional two-phase-flow program is operational and is currently being utilized. A two-dimensional two-phase-flow program is presently being checked out.

(U) Investigations to characterize the BATES exhaust plume utilizing an ion probe and laser are planned for late spring. The measurement of oxide particle velocity will be determined and possibly oxide particle size distribution utilizing the laser technique. The goal of the ion probe is to characterize the exhaust plume of solid motors past the exit plane.

(U) Combustion of Metallized Systems (COMETS)/Project 305901AMT/ Capt C. E. Payne (RPMCP)

(U) During this period, primary buildup for the examination of solid propellant combustion properties has been completed. The research effort is being conducted at the Propellant Evaluation Facility at the AFRPL. A motor firing cell is presently being completed for the investigation of solid propellant combustion in a motor environment. The combustion tests to date have been performed in a small (12.5 cubic inch), high pressure, Rohm and Haas combustion bomb. The primary mode of data collection has been through high-speed cinematography. A summary of the combustion tests performed to date is contained in the following paragraphs.

(U) The problem of flame spread in cracks in solid propellants was investigated. Small samples of propellant with controlled-width cracks were burned under pressures representative of a motor environment. Although a nonflow environment was utilized, quantitative data were obtained. It was determined that under the conditions of these tests, there is a lesser tendency for flames to spread down cracks as the crack width increases. Conversely, the flame spread rate down the crack is more rapid for narrower cracks. In all cases the flame spread rate down the crack was greater than the normal burning rate for most practical propellants.

(U) Preliminary combustion efficiency tests were run on UTP 3001 and TPH 1011 propellants. These tests were primarily designed to optimize photographic techniques. Reliable, usable, photographic records can now be obtained as a matter of routine.

(U) Preliminary investigations were performed relative to the evaluation of methods to command-control the normal burning rate of solid propellants. Approaches which are currently being evaluated are the utilization of

high-voltage electrostatic fields and the external addition of materials which are catalytic to solid propellant burning. The results of this effort are preliminary to date and will be reported in detail in a subsequent report.

(U) The investigation of solid propellant ignition has been at a low level during this reporting period. Operational difficulties with the arc-image furnace have precluded obtaining data. The device is expected to be made operational within the next reporting period.

(U) Exhaust Plume Interference Characterization (EPIC)/Project 305901AMB/
J. Taska, SSgt R.E. Richter (RPMCP)

(U) The primary objective of EPIC is to characterize Air Force propellants with respect to attenuation and modulation of electromagnetic signals when these pass through the exhaust plume.

(U) Preliminary data collected during this report period uncovered three problem areas:

1. Radar beam focusing was poor. This situation has been improved somewhat by moving the radar horns closer to the plume axis. A separation of 7 feet was judged to be a safe minimum for the 70-lb BATES motor. This separation distance results in a spot size of 9 to 10 inches for x-band and 3 to 4 inches for k-band. Reducing the spot size further would require the purchase of new radar horns.

2. Data showed vibration noise. Attempts to eliminate this noise signal by shock and vibration mounting of the microwave equipment have been only partially successful. Efforts in this direction are continuing.

3. Dynamic range of the data-acquisition system was not sufficient. Attenuation greater than 25 db could not be measured. This range has been extended. The new upper limit of our attenuation-measuring capability is now determined by the noise in the system (electrical pickup). A final figure for this limit has not been established at this time.

(U) Remaining activity was centered on buildup of other EPIC systems, specifically the RATS (Radar Additive Test System) and the slant-angle systems.

(U) The slant-angle system consists of an unfocused x-band transmitter with a set of receivers. Each receiver is set at a different angle with respect to the plume axis. Both 70-lb and 15-lb BATES motors will be monitored. This capability is practically complete.

(U) The additive program (RATS) will utilize uncured propellant with selected additives mixed in. These different formulations will be layered in a vertical motor, one on top of the other. Up to five formulations can be examined in a single firing.

(U) The microwave system for RATS consists of two complete microwave systems (x- and k-band), both unfocused. Only attenuation measurements will be performed. This system is also practically complete - only checkout remains.

IN-HOUSE LABORATORY PROGRAM

(U) Advanced Solid Propellant Aging Program/Project 305901HMA/
Lt A.E. Karabela, R. Dolle, and TSgt T. Norton (RPMCP)

(U) A number of high-energy fuels, oxidizers and binders have been proposed for use in solid propellants. The aging characteristics or storability of propellants containing these materials have not been fully described. Physical and chemical tests orientated towards aging properties can provide a realistic estimate of propellant service life. Such estimates have become extremely important in deciding on the future use of these energetic propellants.

(U) The objective of Project Aging is to describe the aging characteristics of the following high-energy solid propellants.

(1) Aluminum hydride (AlH_3) composite propellant.

(2) Hydroxylamine perchlorate (HAP) oxidized composite propellant.

(3) Hydrazine diperchlorate (HP_2) oxidized composite propellant.

(4) Aluminum hydride (AlH_3) double-base propellant

(5) PBEP/TVOPA, AP, aluminum, propellant

(6) PBEP/TVOPA, AP, AlH_3, propellant

Details of propellant formulations as well as laboratory and ballistic tests being performed can be found in the AFRPL-TR-68-24, January 1968, entitled "High-Energy Solid Propellant Aging Study".

(U) During this report period (1 July 1967 to 1 January 1968) there are no technical results to report as the project was in the buildup phase. This phase entailed construction of storage, conditioning and cutting-milling facilities. Included was an extensive buildup of laboratory test equipment. Some baseline data was obtained on the subject propellants during this period. This information is listed in the AFRPL Technical Report cited above.

(U) Solid Propellart Mechanical Behavior Investigations/Project 305902AMF/ D. Saylak, Lt S.W. Beckwith (RPMCB)

(U) Fracture Studies (EPR) - Lt S.W. Beckwith. A literature survey was conducted to find out what work has been done with Electron Paramagnetic Resonance spectroscopy in relation to irradiation and fracture initiation. Fabrication of the loading rig for the EPR fracture studies was completed and the unit was put into operation early in July. Constant-strain-rate tests were initiated on SBR and SBR-Glass Bead formulations furnished by the California Institute of Technology and the North American Science Center. Initial tests at low strain rates ($0.02 \cdot min^{-1}$) indicate that the concentration of free radicals does not change with strain at room temperature, or the free radicals are recombining rapidly compared to the duration of the testing. The output signal is compared with a ruby standard (Cr^{+3}/Al_2O_3) inserted in the microwave cavity. Any changes in isotropy within the spectroscopic splitting factor will show up in the resonance curve of the ruby.

(U) Network Structure Determination and Glass-Transition Studies - Lt S.W. Beckwith. The glass-transition temperature (Tg), cross-link density (Mc), and sol/gel ratio have been determined for PBAA and CTB binder systems with varying cross-link densities and filler contents of aluminum and ammonium perchlorate. Glass-transition temperature and linear expansion measurements were run on a double-base formulation (extruded) in the axial, radial and tangential directions. The linear expansion in the axial direction was 60% lower than the "in-plane" directions, indicating marked anisotropy. Round-robin tests were conducted on an RTV (silicone) rubber and CTB propellant for the ICRPG Thermal Properties Subcommittee. A Tg of $-82^{\circ}C$ and coefficient of linear expansion of $5.27 \pm .28$ (10^{-5} in/in/$^{\circ}$F) was found for the LPC 0064-61E Structural Test Vehicle (CTPB) propellant.

(U) Volumetric Response - D. Saylak, Lt S.W. Beckwith: No work done during this period.

(U) Creep Studies - D. Saylak. A constant stress (as opposed to constant load) apparatus utilizing the "OPSCAN" technology was completed and testing was initiated using cylindrical end-bonded samples. The "OPSCAN" optically measures the diameter of the specimen and feeds the output to an amplifier where it is squared (converted to an area) and fed into a load readjustment control. The load is adjusted by a hydraulic cylinder such that the load-to-area ratio (stress) remains constant. Once under way, it is planned to investigate the creep properties of three binder systems (PBAA, CTB and Polyurethane) with various filler contents of aluminum and ammonium perchlorate and three cross-link densities. In addition, constant-stress tests will be performed as part of the Cumulative Damage effort.

(U) Effects of Storage at Extreme Temperatures on Mechanical Behavior of High-Burn-Rate Propellant - D. Saylak, Lt S. W. Beckwith. A purchase request for the SRAM propellant was initiated during the past period. The purpose of this program will be to determine the critical hoop strain as a function of temperature and web fraction using 6.0 L/D analog motors. In addition, the influence of vibration on the low-temperature strain capability will be investigated. JANAF specimens will be used to generate failure envelopes, stress relaxation modulus, and uniaxial vibration (5 g's) data on aged and unaged samples. X-ray diffraction samples will be used to resolve the storage times and temperatures necessary to induce crystallization.

(U) Nozzle Materials Application and Design Evaluation (NOMAD)/ Project 305903AMH/R.J. Schoner, D.I. Thrasher and A. Bassoni (RPMCH)

(U) Project NOMAD has two objectives: (1) to create a nozzle design and analysis capability at the AFRPL and use this capability to produce advanced designs and evaluate new materials; and (2) to provide motor firing support to other efforts.

(U) The first task undertaken toward accomplishing objective No. 1 is an evaluation of prepyrolyzed materials for rocket nozzle application. This effort consists of test-firing six candidate materials in two 8.5-inch-throat-diameter nozzles on surplus second-stage Minuteman Motors. Since these materials are characterized by high strengths at elevated temperatures we plan to use the best performing in a nozzle which incorporates a "free-standing" exit cone. The two 8.5-inch nozzles will be fired in February 1968 and an AFRPL Technical Report will be published discussing the results of these tests. In addition to evaluating the materials, detailed computer predictions of their performance will be accomplished in an attempt to evaluate the capability of present techniques for predicting material response. Input parameters for the theoretical model will be determined by laboratory tests on the materials and a correlation of empirical results from several previously fired motors.

(U) The second objective encompasses support to several efforts. Eleven tests were conducted in support of AF 04(611)-11646 and two tests for AF 04(611)-10933 (both contracts evaluate ablative material components). Advanced instrumentation techniques are being developed under F04611-67-C-0015 and F04611-67-C-0118 and will receive motor-firing support from NOMAD. The objectives and results from these efforts are discussed elsewhere in this volume.

(U) Solid Rocket Hardware Evaluation/Project No. 305903AMG/
Capt E.M. Schneider, Lt J. Ellison (RPMCH)

(U) Validity of nozzle design theory and technology is dependent on an acceptable demonstration. The SRHE (Char motor) program provides the necessary equipment and manpower for such demonstrations. Char-motor test parameters are variable in order to provide test versatility. All project test motors are insulated vertical steel chambers which contain uncured solid propellant. When fired, the test motor and propellant represent an end-burning configuration. Eight uncured propellant formulations are available. These uncured propellants provide variable test-duration capability and represent flame temperatures from 5200°F to 6500°F.

(U) Since the SRHE program inception in 1963, problems such as propellant storage, propellant sideburning, variable motor inside diameters, and propellant ballistic property reproducibility have been encountered. Some of these problems have been solved and the solution for others is in sight. A thorough description of the Char-motor concept and discussion of early problem areas and solutions can be obtained from AFRPL-TR-67-247 (not yet published).

(U) Four test motor sizes are available for use in this program. Insulated motor inside-burn-surface diameters are 25 inches, 31 inches, 36 inches, and 84 inches. Utilizing these motors and one of the eight propellant formulations, hardware rated at from 1000 to 60,000 pounds of thrust may be tested. Two six-component thrust stands are being constructed to provide necessary data acquisition capability for advanced thrust-vector-control testing and nozzle efficiency evaluation. A small 8-inch-inside-diameter modified JATO motor mounted on a 1000-pound-capacity thrust stand is utilized for propellant checkout and burn-rate measurement prior to large motor test firings.

(U) The Char motors have been utilized six times during the period 1 July to 31 December 1967. Three tests were made in July on an Arde-Portland, Incorporated variable-area-throat nozzle system. Test objectives were to determine restart effects on a pintle nozzle and to ascertain the magnitude of any alumina deposition problem area. The nozzle and pintle performed very well.

(U) In August, a 2.5-inch-inside-diameter United Technology Center wire-wound tungsten nozzle was fired for the second time. The first test in February 1967 consisted of 60 seconds duration, 700 psi chamber pressure, with a 6800°F flame temperature propellant. The second test consisted of 30 seconds duration, 550 psi chamber pressure, with a 6500°F flame temperature propellant. Again, the wire-wound tungsten nozzle exhibited no erosion.

(U) During October 1967, a Thiokol Chemical Corporation castable carbon nozzle was tested. Test objectives were to evaluate performance of low-cost nozzle exit and entrance materials. The firing pressure-time trace was erratic and side burning possibly occurred. The nozzle eroded badly; however, the contractor is uncertain as to the magnitude of erosion caused by the erratic motor pressure.

(U) The final test conducted during this reporting period was on an advanced FW-4 Scout rocket nozzle. The test objective was to determine the performance of a newly designed ablative throat. The test parameters consisted of a 32-second firing duration, 600-psi chamber pressure with a 5700°F flame temperature propellant. The nozzle performed well and ablated at the average rate of 4½ mils/second.

(U) Approximately 18 JATO tests were conducted during this time period in support of motor operating procedure development and propellant burn-rate verification.

(U) Future work will include thrust stand installation and checkout, paper phenolic insulation sleeve evaluation, and restartable Char-motor development.

IN-HOUSE LABORATORY PROGRAM

(U) Project FAST/Project 305901AMX/B R. Warren (RPMCP)

(U) Project FAST was initiated in October 1967 to study the effect of a new experimental foam material on the burning rate of propellants.

(U) The principal objectives of Project FAST are to determine if a proprietary foam material will accomplish a desired increase in burning rates without disadvantages of other high-burning-rate systems that present explosive hazards, poor processing characteristics, catalyst migration, nonreproducible burn rates, and exceptional cost.

(U) Early test results have shown that a significant problem in ignition must be solved prior to obtaining good reproducible burn rates. The foam is now being tested in 4-inch-long by 2-inch-diameter Rohm and Haas motors using an end-burning configuration. Early successes were obtained with a 1-inch layer of foam propellant below a 1-inch layer of modified RH-P-112cb plastisol propellant. However, two motors using only foam propellant (RH-P-112cb) failed on ignition. Motor burning rates have been obtained using the foam in a modified RH-P-112cb propellant.

(U) Data from an ignition study is now being reduced prior to trying to define the proper size and energy requirement of an igniter for this propellant.

(U) Project ADOBE (Obtain experimental data and establish methods for predicting the distribution of downwind concentrations of pollutant from rocket motor exhausts containing beryllium/Project 305907AMK/ H. E. Malone (RPMMX)

(U) The objective of this program is to acquire and develop techniques applicable both to predicting the downwind concentration of pollutant and to assessing the potential airborne reintrainment hazard associated with ground-deposited aerosols from rocket motor exhausts containing beryllium.

(U) Solid rocket motors in the 100- to 4,000-lb size range were fired over a diffusion grid in Test Area 1-46C. Air samples and surface samples were collected on the diffusion grid and analyzed for total beryllium content. The motors were tested under both stable and unstable meteorological conditions. Air samples, surface samples, and meteorological data were used to establish the time relationships and investigate behavior of the latent tracer material after its release.

(U) Various quantities of propellants were burned on a special test pad located near the focal point of the diffusion grid. These tests were conducted using a method similar to that used for the rocket motor exhaust test, the difference being the mode of pollutant release. Experimental data showed that particle sizes from free-burn test yield larger particle sizes than those produced in the rocket motor chamber. Theoretical analysis indicated that the particle size gravitational effects yielded lesser concentrations of respirable-size particles at comparable distances from motor test sources. This effect provides additional assurances that the toxic exclusion radii from accidents will be less, and criteria can be adjusted accordingly for those operations.

(U) The contamination tests are conducted from 2 to 24 or 48 hours after the release of beryllium tracer material to determine the level of area contamination and its relation to the source type, strength, and meteorological parameters. The tests are conducted similar to the other types of tests, except that no actual release of a pollutant will be made.

(U) The 100- to 4,000-lb solid rocket motors provided motor performance data and nozzle evaluation data as well as diffusion data. Since September 1964, 64 solid rocket motors have been test-fired. These include two 1150-lb Thiokol surveyor motors, one 400-lb Hercules motor, one 200-lb Lockheed motor, one 200-lb Hercules motor, one Aerojet 600-lb XM86 motor, ten 600-lb Aerojet ADOBE motors, one 3350-lb NOTS motor, fifteen 4,000-lb Thiokol ADOBE motors, twenty-five 100-lb Aeronutronic motors, one 2,000-lb Hercules motor, and two 6,500-lb Skybolt (aluminum) motors. Sixteen of the Aeronutronic motors and one Skybolt motor were fired under stable meteorological conditions (i.e., inversion layer). Thirteen contamination tests were conducted and six burn tests. Approximately 20,000 beryllium air samples, 500 surface samples, and 500 hydrogen chloride gas samples were collected. The ADOBE diffusion crew also supported a BSD-Aerojet-General Corporation 11,000-lb motor beryllium test in Lovelock, Nevada in May 1967. Air samples were collected out to 15 and 30 miles from the motor source. Approximately 250 beryllium and 250 HCl samples were collected. The beryllium concentration was approximately the amount predicted from the diffusion equations (derived from 30 of the above firings) which were extrapolated out to 15 and 30 miles. Still to be conducted are 10 to 15 contamination tests. This will involve collecting of 200 air samples and 25 to 50 surface and soil samples per test.

(U) Project PYRO (Liquid Propellant Blast Hazard Program)/Project 921000AMU/R. L. Thomas (RPMMX)

(U) The objective of the NASA/USAF/AEC-sponsored liquid propellant blast hazard program is to develop a reliable method for predicting the blast and thermal environment which may be experienced from an accidental explosion of liquid propellants during launch or test operations of military missiles or space booster vehicles. The propellant combinations being investigated are N_2O_4/50% UDMH-50% N_2H_4, LO_2/RP-1, and LO_2/LH_2. Approximately 234 tests are planned using 200-lb, 1000-lb, and 25,000-lb total propellant weight test articles.

(U) Test activities began in June 1964 and to date a total of 279 tests have been completed (one-hundred-eighty-one 200-lb, thirty-four 1000-lb, eleven 25,000-lb, one full-scale S-IV, and fifty-two explosive calibration tests). During the reporting period five 25,000-lb 30-foot-drop tests were conducted. One 25,000-lb LO_2/LH_2 30-foot-drop test, three 1000-lb LO_2/LH_2 30-foot-drop tests, three 1000-lb LO_2/RP-1 with 200-lb LO_2/LH_2 30-foot-drop tests, one 25,000-lb LO_2/LH_2 confinement-within-the-missile test, and two full-scale first-stage Titan I confinement-within-the-missile tests will be conducted during the January to March 1968 time period.

TECHNICAL SUPPORT GROUP
(INSTRUMENTATION, FACILITY PLANNING)

LIST OF ACTIVE CONTRACT PROJECTS

TECHNICAL SUPPORT GROUP (RPF)

(U) Prototype Vapor Detection Device for Atmospheric Sampling and Analysis for Fluorine and Hydrogen Fluoride/Parametrics, Inc., Waltham, Massachusetts/A. Cucchiara/AF 04(611)-11409/ A.H. Boyd (RPFTR)

(U) The objective of this program is to provide a vapor detector which will sample and analyze the atmosphere for toxic fluorine and hydrogen fluoride vapors in the presence of each other and other interfering vapors found in the vicinity of rocket test operations. The detector will provide immediate analysis of atmospheric samples to insure that toxicity level of F_2 and HF is within the safe limits established for human exposure.

(U) The approach being used employs kryptonated solid material which reacts specifically with the vapor being detected. This reaction releases the radioactive krypton gas which is detected with a radiation detector. The count rate is proportional to the krypton gas released which is proportional to the toxic vapor concentration.

(U) The contractor has delivered a prototype fluorine-hydrogen fluoride detection system using a kryptonated clathrate sensor material to detect fluorine, and a kryptonated silicon sensor material to detect hydrogen fluoride. The prototype system is a battery-powered sampler-analyzer which has been demonstrated to be selective to fluorine and hydrogen fluoride. The sensitivity of the detector has not been completely evaluated because of noise within the solid-state radiation detectors. Initial data indicates that the contract objectives of detecting fluorine in the 0.5- to 10-ppm range and hydrogen fluoride in the 2.5- to 50-ppm can be accomplished when improved solid-state radiation detectors are installed. This will reduce the noise input to the electronic counting system and will upgrade the performance to comply with program objectives.

(U) REFERENCE

"Detection Techniques for Hazardous Vapors of Elemental Propellants" Tech. Doc. Report ASD-TDR-63-294, July 1963.

(U) Development of Propellant Field Kits/Thiokol Chemical Corp., Reaction Motors Division, Denville, New Jersey/ F. Hoffman/ AF 04(611)-11531/H. Martens (RPCCR)

(U) The objective of this task is to develop field techniques for the quality control of liquid storable propellants and auxiliary pressurizing gases. At the present time samples are sent from field locations to a laboratory for analysis. The time required for analytical result acquisition does not exclude the utilization of contaminated propellants. Therefore, the development of acceptable field-test kits will enable crews (trained, nontechnical personnel) to determine the need for further detailed analysis in only those few cases where marginal quality may be indicated. The time saving will improve significantly the readiness posture of operational liquid propellant missile systems.

(U) The current 20-month program (12 months plus an 8-month funded extension) utilized a four-phase approach.

Phase I consisted of contractor-conducted studies to correlate analytical methods with field-use criteria. Candidate methods were selected for incorporation into field kits to perform the following tasks as listed below:

Propellant	Quality Control Parameters
UDMH/N_2H_4, 50/50	UDMH-N_2H_4 ratio, moisture particulates
N_2O_4/NO, 90/10	NO content
N_2O_4, 100%, or N_2O_4/ NO, 99.5/0.5	particulate, moisture

Phase II consisted of contractor-recommended procedures which were laboratory-tested in a breadboard apparatus. Upon approval by the AFRPL project engineer, these were incorporated into prototype kits.

In Phase III these prototype test kits are to be evaluated and modified as necessary. Calibration techniques are to be perfected and manuals are to be prepared. Drawings and design specifications are to be generated.

Phase IV will consist of a demonstration and evaluation period at AFRPL under field conditions. The time is not to exceed 15 working days.

(U) During the first 12 months of the contract the following three test kits were completed through Phase III:

1. UDMH/N_2H_4 - determines moisture
2. UDMH/N_2H_4 - determines N_2H_4 and the UDMH-N_2H_4 ratio
3. N_2O_4/NO, 90/10 - determines NO content

The above phase was completed in June 1967. For the 8-month redirection, the original heterogeneous propellant, Alumizine, was dropped from consideration, and particulates in UDMH/N_2H_4 and N_2O_4 and the moisture equivalent in N_2O_4 were added. Phase IV of the contracted effort should begin during the latter part of January or early part of February 1968. No unusual technical difficulties have been encountered.

(U) REFERENCES: <u>Field Testing of Propellants</u>

Quarterly Reports

AFRPL TR-66-121	June 1966, AD 434486
AFRPL TR-66-218	September 1966, AD 489411
AFRPL TR-66-333	December 1966, AD 804312
AFRPL TR-67-76	March 1967, AD 810813

(U) Transient Flow Calibration System/Engineering Physics Company/ W. L. Danek/AF 04(611)-11622/A. H. Boyd (RPFTR)

(U) The objective of this effort is to provide a Pulse Flow Calibration System for accurate calibration of flowmeters used to measure propellant flow to pulsed attitude-control rocket engines. The flow calibration system will generate pulsed flow of actual rocket propellants and oxidizers.

(U) The approach being investigated utilized a positive displacement technique with the liquid placed on a closed-loop system with two cylinders back-to-back. As the pistons are moved the liquid is moved from one cylinder through the flowmeter to the other cylinder, thus placing the liquid under positive pressure in either flow direction. A high-response Servo drive system moves the piston in response to electrical input signal. A digital displacement measurement system and an analog velocity measurement system are attached to the pistons to measure the actual flow rate, rise time and volume of liquid displaced.

(U) The contractor has completed the design and fabrication of the Transient Flow Calibration System utilizing a stepping motor drive system. This drive technique was technically unacceptable. The rise-time requirements were not met. The drive system was then redesigned to use a closed-loop Servo drive system which has produced a rise time of 2 milliseconds with a 5% overshoot. The overshoot damped to less than 2% in 2 milliseconds. This performance was measured with water in the system. The performance will be checked using propellant or propellant simulates at the AFRPL. The equipment will be delivered to AFRPL for installation and final evaluation at the end of February 1968.

(U) AFRPL Micrometeorological System/Gulton Industries/R. Groush/ AF 04(611)-11807/W. C. Severin (RPFT)

(U) The objective of this program is to design, fabricate and install a meteorological system to support the firing of motors which use toxic propellants. Under computer control, meteorological data is automatically collected from sensors covering an area of approximately 100 square miles. The data is processed by the computer, displayed on a panel, and predictions of toxicity concentrations are made.

(U) The system is installed and it is anticipated that it will be completely operational by 1 March 1967. Only minor difficulties have been experienced during a 60-day operational checkout period. System performance is acceptable, and represents several advancements in the state-of-the-art, notably those of accuracy and inexpensive long-distance-data transmission.

(U) REFERENCE:

Ocean Breeze and Dry Gulch Diffusion Programs, AFCRL-63-791, Volumes I and II.

(U) High-Response Laser Flowmeter/Sperry Gyroscope Company, Great Neck, New York/J.R. Schneider/F04611-67-C-0055/A.H. Boyd (RPFTR)

(U) The objective of this program is to provide two flowmeter systems using the ring laser technique for the accurate measurement of the instantaneous propellant flow rate to attitude-control rocket engines during test at simulated altitude of 600,000 feet.

(U) The approach utilizes the Fresnel drag effect to produce a frequency-mode split in a ring laser. The continuous laser oscillations in the ring laser traveling clockwise (cw) and counterclockwise (ccw) are independent, except that they share the same cavity structure and are correlated in frequency. The frequency shift of the cw and ccw waves are in opposite directions due to differential-phase delays produced by the moving media within the laser cavity. The resultant split frequency is proportional to the velocity component along the optical axis of the flowing media. This technique provides a very high-response flowmeter in which the flow is not disturbed by the measurement technique.

(U) The scope of the contract was increased to provide two additional flowmeters. One of the additional flowmeters will be designed to measure chlorine pentafluoride and the second will measure hydrazine fuels. Optical loss measurements have been made on nitrogen tetroxide and chlorine pentafluoride oxygen and hydrogen, MMH and UDMH-Hydrazine fuels. A breadboard laser flowmeter system was evaluated and the final configuration for the prototype flowmeter selected. Parts for the flowmeters have been fabricated and the first two flowmeters are in operation. Initial testing of the prototype flowmeter identified technical difficulties with power modulation of the laser. Investigation of the technical difficulties has been completed, corrective measures have been taken, and system testing is currently in progress. Delivery of all four flowmeters is scheduled for April 1968.

(U) REFERENCE:

High-Response Laser Flowmeter, Phase I Technical Report, Sperry Gyroscope Co., AD 818681, April 1967.

(U) Particle Velocity Measurement in Gas-Particle Two-Phase Flow (Solid Rocket Exhaust) by Laser Doppler Techniques/Stanford University/ Dr. Howard Seifert/F04611-67-C-0056/A. H. Boyd (RPFTR)

(U) The objective of this program is to obtain formal criteria for the design of equipment to measure the number and velocity of micron-size particles flowing in the exhaust of rocket propulsion systems.

(U) The approach being investigated measures the doppler shift in laser light reflected from particles in its focus field and, in addition, counts the number of particles traversing its focus field. Since the focus field is small, the number velocity distribution can be explored by moving the focus field through the exhaust stream.

(U) The contractor has designed and fabricated an apparatus to measure the velocity of particles in rocket exhaust. The optical and electronic packages have been tested and one rocket motor test was conducted. This test did not produce usable data because of technical problems with the mirrors in the Fabry-Perot interferometer. These mirrors are now replaced and additional tests will be conducted using 1-, 3- and 8-inch-exit-diameter rocket engines. Theoretical analysis of the data and data-processing techniques are continuing. This effort is directed to measuring particle size and size distribution in addition to measuring the velocity and velocity distribution. An investigation of light attenuation due to the particle cloud indicates that the laser light probe can penetrate the exhaust plume to obtain useful data in an 8-inch exit-diameter rocket engine.

(U) REFERENCES:

a. Application of a Laser-Doppler Technique to the Measurement of Particle Velocity in Gas-Particle Two-Phase Flow. AFRPL-TR-66-119, June 1966, AD 802976.

b. Development of a Laser Velocimeter System. AEDC-TR-67-175, October 1967.

(U) Development of an Electrostatic Probe System/AeroChem Research Laboratories, Inc., Princeton, New Jersey/Dr. Walter Maise/ F04611-67-C-0059/H.I. Binder (RPFTR)

(U) The objectives of this program are to develop a probe which will withstand the rocket engine exhaust plume environment while retaining a high electrical resistance and to predict and measure electrical currents flowing through the ionized gases within the plume. The information generated is to be correlated with radar attenuation measurements.

(U) The contractor has completed Phase I of this effort which includes studies to predict and measure ion concentration within Laboratory burner flames. Small-scale rocket engine tests have also been conducted with experimental probes at the Naval Research Laboratory, Washington, D.C. A successful probe for use in the nonsupersonic regions of exhaust plumes has been developed. Efforts to correlate predicted ion concentration with radar attenuation measurements are in progress.

(U) In approximately 2 months, tests will be conducted at AFRPL using larger engines, and the contractor will thereafter prepare a final report. Meanwhile, consideration is being given to the solution of two major problems, namely: the prediction of ion concentration in the supersonic region of the exhaust; and the problem of aluminum deposition on the surface of the electrostatic probe.

(U) REFERENCES:

a. Ionization in Rocket Exhausts, W. W. Balwanz, Tenth International Symposium on Combustion, The Combustion Institute, 1965.

b. Determination of the Electrical Characteristics of Rocket Exhaust Plumes with Electrostatic Probes, Progress Report, 1 January to 30 June 1967, AeroChem Research Laboratories, Princeton, N.J., AeroChem TN-110, July 1967.

c. The Use of Ionization Probes to Determine Rocket Motor Parameters, AeroChem Research Laboratories, Princeton, N.J., AFRPL-TR-65-208, November 1965, AD 474517.

(U) AFRPL Development of a High-Response Differential Pressure Transducer/Electro-Optical Systems, Inc., Pasadena, California/ Julian Delomonte/F04611-67-C-0090/H. Binder (RPFTR)

(U) The objective of this program is to develop a differential pressure transducer with high-response, high-common-mode pressure rejection and high static accuracy. This pressure transducer is required to upgrade the response on a hydraulic pulse thrust-measuring system. The specific requirements include a differential pressure range of 0 to 10 psid, flat-frequency response to 1200 hz and a common mode rejection of less than ±1 percent full-scale for a line pressure change from 0 to 1000 psig.

(U) The program is divided into three phases. The first phase involves an analysis and experimental program to quantitatively define all factors influencing measurement of differential pressure. The second phase is design, fabrication and test of a prototype transducer. Phase three is fabrication and test of two modified and refined transducers.

(U) Phase one of the program is complete (see Reference a) and phase two is 90 percent complete. Preliminary test results of the transducer indicate that all major objectives of the program will be met.

(U) REFERENCES:

a. Development of a High-Response Differential Pressure Transducer, Phase I, AFRPL-TR-67-268, October 1967, AD 821896.

b. High-Response Low-Level Pulse Engine Thrust Stand System, AFRPL-TR-66-344, December 1966, AD 804596.

(U) AFRPL Ablation Measurement/TRW Systems Group, Redondo Beach, California/H. Lurie/F04611-67-C-0115/W. L. Buchholz (RPFTR)

(U) The object of this program is to develop an ablation and erosion rate measuring system compatible with Minuteman second-stage nozzles. The measurement system is to be used to provide measurements of ablation and erosion rates to verify rates predicted by a computer program which models the rocket nozzles' performance.

(U) The approach being investigated involves a follow-on to a feasibility study which was completed in April of 1967 and is reported in the reports listed in References a and b.

(U) The technique involves the imbedding of radioisotope-seeded needles in the ablation material to provide a dual ablation measuring system. This system is to measure simultaneously the material surface recession rate and char interface recession rate during ablation of carbon-cloth phenolic (MX 4926), paper phenolic (FM 5272), asbestos phenolic (MXA 6012) and pyrolyzed-carbon-reinforced phenolic. The system is to operate on the principle that two radioactive compounds which produce gamma radiation of significantly different energy levels, compatible with virgin material and char material, are incorporated into the ablative material. Two isotopes are to be selected for each nozzle liner material so that depletion rate of the other will correspond to the recession of the char-virgin phase interface. A radiation detector capable of differentiating between energy levels as well as counting rates will monitor the radiation from each of the two isotopes. The rate of change of counts from each isotope will provide a continuous measure of both surface recession and char interface recession rate.

(U) During this reporting period the isotopes were selected, a systems analysis was performed, the detection instrumentation system was designed and procured and preliminary laboratory scale tests were performed.

The laboratory tests consisted of subjecting test nozzle materials installed with isotope-seeded needles to simulated rocket motor test firing conditions. Preliminary test results indicated that the measurement system will measure erosion and char rates to within $\pm$ 0.010 inches resolution.

(U) Future plans consist of test firing the measurement system in two Minuteman second-stage motors. The results will be used in direct support of an in-house AFRPL Nozzle Evaluation Program.

(U) REFERENCES:

a. Feasibility Demonstration of a Rocket Engine Ablation Gauge, Task II Summary Report, AFRPL-TR-67-218, August 1967, AD 820349.

b. Feasibility Demonstration of a Rocket Engine Ablation Gauge, Task III Summary Report, AFRPL-TR-67-235, October 1967, AD 821304.

c. Feasibility Tests of a Radioisotope-Type Ablation Measuring System, J. Dempsey and P. Poleshuk, Plenium Press, New York (1966).

d. Heat-Shield Ablation Measurements using Radioisotopes Techniques, G.W. Brandon, Jr., NASA TND-3329, March 1966.

e. Determination of Heat-Shield Char-Front Recession with a Nucleonic Technique, W.G. Davis, NASA TND-3264, March 1966.

(U) Ultra-High-Temperature Indicating System/Aerojet-General Corporation, Sacramento, California/J. DeAcetis/F04611-67-C-0118/H.I. Binder (RPFTR)

(U) The objective of this program is to develop a temperature-indicating system to measure the temperatures within rocket nozzle ablative liners in the temperature range of 4000°F to 6000°F where thermocouples become inoperative.

(U) The approach being pursued is to implant minute temperature-sensitive pellets of refractory materials and their carbides into the ablative materials. The pellets are encapsulated within a carbon sheath. Posttest analysis will indicate whether or not melting has occurred in the pellets, thereby establishing a temperature which has been exceeded. The use of pellets of varying eutectic composition will bracket the actual temperature attained within 50°F.

(U) The contractor has extensively searched the literature for any related methods, and it appears that this is a unique and novel effort. Extensive study has facilitated the selection of only binary refractory metal eutectics. Laboratory tests have been run on many of the eutectics to accurately establish their melting points.

(U) The finished instrumented plugs of ablative material will be installed in nozzles at the AFRPL during April or May of 1968, and the posttest analysis will be conducted by the contractor to establish the temperature profiles near the surface of ablative nozzle liners.

(U) REFERENCES:

a. Development of an Ultra High Temperature Indicating Sensor for Use in Ablative Rocket Nozzles, Phase I Report, AFRPL-TR-67-284, October 1967.

b. Measuring Temperature, L. G. Rubin, International Science and Technology, January 1964.

(U) Pressure Sine-Wave Generator System/Standard Controls, Inc.,/ F. Notman/F04611-68-C-0009/C.M. Richey (RPFTR)

(U) The objective of this program is to develop and fabricate a prototype pressure sine-wave generator for use in the dynamic calibration of pressure transducers and end-to-end data acquisition systems normally used in rocket engine test programs. The generator shall have a frequency range of from 40 Hz to 15,000 Hz and a dynamic pressure range of from 0 psi to 100 psi with a static pressure level up to 2000 psi.

(U) The approach being used in this effort is that of a bimorphic piezoelectric crystal in an enclosed chamber. Sinusoidal high voltage (1000 volts) is used to drive the crystal and the chamber is designed to minimize distortion. This crystal driver unit is the basis of the Sinusoidal Pressure Generator (SPG) system. Added to the system will be all those components necessary to fulfill the requirements of this effort, such as monitor transducers and equipment, sine-wave-function generator, distortion analyzer, oscilloscope, etc.

(U) Much time has been spent in the final design of the SPG driver unit. A study to determine the best monitor transducer has been completed and several modifications have been accomplished to the pressure chamber of the SPG driver to insure low distortion. The final design of the driver unit is presently underway. Dynamic pressures from 50 psi to over 200 psi have been achieved over a frequency range exceeding 16,000 Hz.

(U) REFERENCE:

Operation Manual for the NOTS-NASA Rocket Motor Acoustic Test Facility Steady State Resonance Tests with Flow; F.G. Buffum; U.S. Naval Ordinance Test Station, China Lake, Calif.; NOTS TP 4304; June 1967.

IN-HOUSE LABORATORY
TECHNICAL REPORTS PUBLISHED

IN-HOUSE REPORTS

AFRPL-TR-67-203 - Measurement of the Exhaust Composition of Selected Helicopter Armament (Project West)/August 1967/Unclassified Report/AFRPL, Edwards, California/P.B. Scharf, B.B. Goshgarian and H.M. Nelson

AFRPL-TR-67-213 - Exploratory Propellant Chemistry Semiannual Report/September 1967/Unclassified Report/AFRPL, Edwards, California/ Dr. W.C. Solomon, Dr. J.A. Blauer, and F.C. Jaye

AFRPL-TR-67-256 - Propellant Specifications, Preparation and Use/ October 1967/Unclassified Report/AFRPL, Edwards, California/F.S. Forbes

Unclassified

Security Classification

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13. ABSTRACT

(U) This report describes the status and significant progress of each AFRPL contract and in-house laboratory program for the time period of 1 July 1967 to 31 December 1967.

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